VOL. X. 1906

# TRANSACTIONS
OF THE
# AMERICAN ELECTROCHEMICAL SOCIETY.

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# TRANSACTIONS

OF THE

# AMERICAN ELECTROCHEMICAL SOCIETY

157533

## VOLUME X.

## TENTH GENERAL MEETING

NEW YORK, OCTOBER 8 AND 9, 1906.

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VOLUME X. 1906.

# TRANSACTIONS

OF THE

# AMERICAN ELECTROCHEMICAL SOCIETY

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## PROCEEDINGS

CONDENSED MINUTES OF THE TENTH GENERAL MEETING OF THE SOCIETY, HELD AT COLUMBIA UNIVERSITY, NEW YORK, OCTOBER 8 AND 9, 1906.

(Number of members registered, 32; guests, 6; total, 38.)

### SESSION OF OCTOBER 8th.

The meeting was called to order at 10 A. M., at Havemeyer Hall, Columbia University, President Hering in the chair.

Prof. C. F. Chandler, representing Columbia University, was introduced by President Hering, and asked to say a few words to the members of the Society.

PROF. CHANDLER: Mr. President and fellow members of the youngest scientific organization which I think we have in this country, and I think the organization which is going to prove, if possible, the most important; it gives me great pleasure to welcome you to Columbia University.

I have not prepared any speech to make to you. I was simply asked to extend a welcome; but there are many ideas that naturally associate themselves with electrochemistry. It has already worked such a revolution in many branches of chemical industry

that it seems destined to change entirely the character of a large proportion of chemical operations which we have in the past been obliged to bring about by the direct aid of heat and by the direct application of the most strenuous physical exertion on the part of the workman.

It really is a great pleasure to enter into one of our electro-chemical establishments and to draw the comparison between what one sees there and what one saw formerly in great establishments where similar results were obtained.

In old times in the handling of metals, heat was the agent; terrible heat; scorching furnaces; workmen obliged to strip to the skin, handling enormous heavy rakes and hoes, and push them into those terribly hot furnaces to rake the molten metal, expending their physical energy to an exhausting degree and heating their poor bodies until they became feverish. Now, you go into an establishment like the Pittsburgh Reduction Company's works and there is hardly anything to do. Still more striking, if you enter the works of the Castner Company, where sodium is being manufactured, or the Saltville Company's works at Niagara Falls, where caustic soda is manufactured. Those works illustrate the change better than any others.

In old times soda was made by treating salt with sulphuric acid, and then the sulphate of soda had to be mixed with carbonate of lime and coke, and worked over in reverberatory furnaces under the most tiresome conditions. Now, the salt solution circulates automatically to a series of tables. The dynamo, worked by the power of Niagara Falls, furnishes the current and everything is automatic; and all the workman has to do is once in a while when one of the cells get out of order, to take the cover off and repair it again. Instead of being a hard work it is really a pleasure for the workmen, and they ought to be willing to pay something for the privilege of working in a factory of this kind.

The aluminium factory is another illustration of the wonderful effect of electro-chemistry in accomplishing economical results. You are all familiar with that industry and know how many different processes were attempted and how strenuous many of them were and how dangerous some of them were on account of the possibility of explosion. And then Charles M. Hall, of Oberlin College, came into the field and put his young mind on the

problem of making aluminium and studied it and came to the conclusion that the only way was to make use of a solvent for alumina, free from water. He graduated and continued his studies, and but a very short time elapsed before he hit upon the only practicable way of accomplishing this result in the best way that has so far been discovered. He found that melted cryolite would take up alumina to the extent of 25 per cent. of its weight, although Rose, one of the greatest chemists who ever lived, had experimented with cryolite and had actually extracted aluminium from cryolite; but had failed to observe that cryolite was a solvent for alumina; and when St. Claire Deville established his aluminium works in France, he actually united his globules of alumina by using, among other things, cryolite as a flux to clean the surface of those globules, and yet he did not discover that it was a solvent for alumina, and it remained for this young college student to start out to find a solvent and to discover that melted cryolite was an admirable solvent for alumina.

And the next step was whether he could electrolyze the aluminium out of this solution. And he found that it could be done without any difficulty whatever, and on reducing the discovery to practice he found it was not necessary to apply any external heat; that the heat developed by the passing of the current was all that was necessary to maintain the fusion of the cryolite. And so this problem, which had engaged the attention of scientific chemists for over fifty years, was solved by this youth so successfully as to make aluminium a rival of copper in the industries.

And the simplicity of the whole thing; these so-called pots, receive their proper current of electricity and they receive a proper addition of alumina from time to time and the process goes on from hour to hour; and every morning each one of these pots you might say is milked like a cow, and they tap the milk, one hundred pounds of aluminium out of each of these pots that has been liberated by the current, and all the workmen have to do is to run about from time to time and put in a little more alumina.

I do not know how much Mr. Hall is in the way of telling of the operations of those furnaces; but there are one or two things which I think I may tell without violating any confidence. Of course, that melted cryolite is very hot and it is very scorching to the workmen, and in looking after some way to protect the

men from the heat, the remarkable discovery was made by Hall that when pulverized coke was put on the melted cryolite it does not wet it. The pulverized coke sheds melted cryolite just as a duck's back sheds water, and no matter how much you stir the coke up with the melted cryolite it always comes up to the top and is dry and black, and that preserves the heat and serves as a comparative non-conducting barrier between the heat and the face of the workmen.

The alumina can be sprinkled on top of that pulverized coke and lie there until it is wanted, and the heat is sufficient to thoroughly dry it. And then Hall invented a most ingenious scheme to find out when the bath required more alumina. Hall put a little incandescent electric light in circuit between the cathode and the anode. The lamp requires about twenty volts. It only takes about seven volts of current to overcome the resistance and electrolyze the alumina. So as long as the bath contains alumina, the lamp fails to emit any light. But when it is necessary to introduce more, then the resistance rises and it takes over twenty volts to carry the current through. That, of course, is sufficient, for the lamp which flashes and the workmen who are always on the watch sing out "There she blows," and the workmen immediately hurry to that particular pot and all they have to do is to stir the alumina on top of the coke into the bath and everything goes on smoothly.

This is the thought that came into my mind as I was invited to say something to you; the wonderful effect of electro-chemistry in simplifying these metallurgical operations, of accomplishing the same results in a great deal better way and saving the expense of the wear and tear on the human beings who are obliged to watch the apparatus and the machinery.

I think therefore, it is a very valuable addition to our professions to have electrochemistry as a special combination of chemical with physical science and engineering.

Of course, every time a new association of this kind is formed, the members of the old association are a little sorry. When we proposed to have a Chemical Society, the old Lyceum of New York was very unhappy about it. A few devoted men had been struggling along for years in New York City to encourage an interest in science, and a few devoted scientists had been in the

habit of meeting in a little room downtown and calling themselves the Lyceum of Natural History. Of course, as the name indicates, they devoted their time chiefly to discussing bugs and every kind of animal and plant, and the chemists did not find it particularly interesting. The chemist would deny himself some social entertainment and go down and meet a dozen enthusiastic zöologists, and they would talk about the difference in the shapes of clam shells from different parts of Long Island; and so the chemists concluded that it would be a good thing to have a chemical society, and they were lachrymose in the other society. They felt we were deserting the flag. And when the Electrochemical Society was started there were some tears shed in the Chemical Society for fear that it would diminish interest in our society; but I do not think it will have that effect.

You know the English people who celebrated the jubilee of Sir William Perkin, were very unhappy when they heard we were going to have a jubilee over here. They said, "Come over to England." Well, very few people could go to England for that purpose. They became reconciled, however. When we were going to have a jubilee here, the Boston chemists thought they would not come here, but have a jubilee in Boston. We were a little disappointed at first, but we said afterwards, it is all for the good of the cause, which is to honor Sir William Perkin, and to magnify the importance of chemistry. Whenever we can get together in any locality whatever, it helps the cause, and the more societies of this kind that we can have the better it is for the cause of science; the value of science will be more thoroughly recognized and support will be given to scientific and educational enterprises; so, as one of the earliest members of the American Chemical Society, I congratulate you gentlemen on having united to form an Electrochemical Society, and I am proud to have become a member of it, and I welcome you to Columbia, and the oftener you come and the longer you stay, the better we shall like it. (Applause.)

The President: In the name of the Society, I thank Professor Chandler, for his kindness in extending the hospitality of Columbia University to this Society by inviting us to hold this meeting in its halls.

The following papers were then read and discussed as printed in full in the Transactions:

"Formula for the E. M. F. of a Helmholtz Concentration Cell," by Prof. Henry S. Carhart.

"Visible Migration of Particles Between Electrodes," by Carl Hering.

"Some Small Laboratory Appliances for Electric Fusion Work," by S. S. Sadtler.

"Copper Cathodes in Nitric Acid," by G. H. Cole.

"Melting Points of Some Cryolite-Alumina Mixtures," by F. R. Pyne.

"Some Factors Affecting the Distribution Laws," by H. E. Patten, Ph.D.

At 1.30 P. M. luncheon was served at Columbia University.

At 2.30 P. M., at the College of the City of New York, Prof. Charles Baskerville delivered a lecture on "Ultra-Violet Light in the Laboratory and in Practice," followed by a discussion.

After the lecture the large Edison Electric Lighting Station, was inspected, where a large number of 5,000 Kilowatt turbine generators and other interesting features were seen.

In the evening a dinner at the Liederkranz Hall was participated in by about thirty-three members, including a few guests.

### SESSION OF OCTOBER 9th.

The following papers were read and discussed, as printed in full in the Transactions:

"Pyrometers, Theoretically and Practically Considered, with Remarks on the Definition of Temperature," by Dr. E. F. Roeber.

"A Thermo-Electric Pyrometer for General Industrial Applications," by F. F. Schuetz.

"The Heraeus Le Chatelier Pyrometer," by Dr. R. Moldenke.

Discussion on Pyrometry, by R. S. Whipple.

Communicated Discussion Descriptive of the Price Pyrometer, by Elec. Dental Supply Co.

Discussion on Special forms of Pyrometers, by R. P. Brown.

"The Decker Primary Battery," by Prof. F. B. Crocker.

After the adjournment of the meeting, experiments with the different Pyrometers were performed.

In the afternoon about thirty members visited the works of the American Smelting and Refining Co., at Maurer Station, near

Perth Amboy, N. J., where Mr. Emerich showed them the large plant for the electrolytic refining of copper, and the Moebius silver refining process, which were of great interest to most of the members who took part in the excursion.

In the evening the members were invited to be present at a smoker given to Sir William Henry Perkin by the chemists of New York City.

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MEMBERS ELECTED JUNE, 1906, TO DECEMBER, 1906.

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August 3, 1906: Edson Ray Wolcott, Golden, Colo.; O. L. Kowalke, Madison, Wis.

September 7, 1906: Harry J. Wolf, Telluride, Colo.

October 6, 1906: A. J. Shinn, Philadelphia, Pa.; Wm. P. Divine, Philadelphia, Pa.; Frank A. Decker, Philadelphia, Pa.

November 3, 1906: John N. Pring, New York; Philip B. Sadtler, Mechanicsville, N. Y.

December 1, 1906: Wm. H. Bristol, Hoboken, N. J.; W. H. Van Winckel, Toronto, Can.; E. R. Berry, Malden, Mass.

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Brown, Prof. W. G., Univ. of Mo.
Schlundt, Herman, 801 College Ave.
Shaw, Prof. H. B., Univ. of Missouri.
**Kansas City.**—
Hofmann, Ottokar, 3002 E. 7th St.
Kent, Jas. M., 2726 Holmes St.

**MONTANA.**

**Corbin.**—Malm, John Lawrence.
**Great Falls.**—
Burns, W. T., Boston and Montana Smelter.
Pyne, Francis R., Boston and Montana Smelter.
Wheeler, Archer E.
**Helena.**—Gerry, M. H., Jr., Missouri River Power Co.
**Polaris.**—Wells, Prof. J. S. C., Silver Fissure Min. Co.

**NEW HAMPSHIRE.**

**Berlin.**—Barton, C. B., Burgess Sulphite Fibre Co.

**NEW JERSEY.**

**Arlington.**—Joyce, C. M., Box 23.
**Boonton.**—
Sergeant, E. M., Gen'l Storage Bat. Co.
**Camden.**—Robbins, W. A., 904 Cooper St.
**Dover.**—Hough, Arthur.
**Dunnfield.**—Keith, Dr. N. S.
**East Orange.**—
Aylsworth, J. W., 223 Midland Ave.
Fliess, R. A., 21 S. Clinton St.
Holland, Walter E., 211 Arlington Ave.
**Elizabeth.**—Addicks, Lawrence, 420 N. Broad St.
**Franklin Furnace.**—Rowand, L. G., N. J. Zinc Co.
**Glen Ridge.**—
Barr, B. M., 50 Lincoln St.
Bristol, Wm. H., Stevens Inst. of Tech.
**Hoboken.**—Stillman, Dr. T. B., Stevens Inst. of Tech.
**Maurer.**—
Colcord, Frank F.
Wesson, David, 111 S. Mountain St.
**Newark.**—
Colby, E. A., Baker Platinum Works.
Gifford, Wm. E., 408 N. J. R. R. Ave.
Thowless, O. M., P. O. Box 273.
Van Winkle, Abr., 35 Lincoln Park.
Walsh, Philip C., Jr., 19 Grant St.
Weston, Edward, Sc.D., LL.D., 645 High St.
**New Brunswick.**—Voorhees, Louis A., 111 Carroll Place.
**Orange.**—Edison, Thomas A.
**Perth Amboy.**—
Easterbrooks, F. D., Raritan Copper Works.
Emrich, Horace H., 142 Water St.
Foersterling, Dr. Hans, Roessler & Hasslacher Chem. Co.
Moses, Herbert B., 174 Brighton Ave.
Philipp, Herbert, 84 High St.
**Princeton.**—Hulett, Geo. A., 2 Murray Pl.
**Upper Montclair.**—Palmer, Chas. S., 637 Valley Road.
**West Hoboken.**—Thomas, Chas. W., 328 Palisade Ave.
**Woodbridge.**—Doney, D. C.
**Woodbury.**—Norman, Geo. M., 75 Aberdeen Place.
**Wyckoff.**—Browne, Wm. Hand. Jr.

**NEW YORK.**

**Albany.**—McElroy, Jas. F., 131 Lake Ave.
**Auburn.**—Case, Willard E., c|o R. L. Janes, 122 Genesee St.
**Brooklyn.**—
Drobegg, Dr. G., 11 Bartlett St.
Gabriel, G. A., 1611 Beverly Road.
Haslwanter, Chas., 86 Pilling St.
Maywald, F. J., 1028 72d St.
Nodell, Wm. L., 243 S. 4th St.
Roller, H. C., 35 Rugby Road.
Sheldon, Dr. Samuel, Polytechnic Inst.
Sperry, E. A., 100 Marlborough Road, Prospect Park, South.
Wiechmann, F. G., P. O. Box 79, Station W.
Wills, J. Lainson, 133 Midwood St.
Wray, Edward, 76 Columbia Heights.
**Buffalo.**—
Bierbaum, C. H., 418 Prudential Bldg.
Devine, Jos. P., 312 Mooney-Brisbane Bldg.
**Clinton.**—Saunders, Prof. A. P., Hamilton College.
**Elmira.**—Carrier, C. F., Jr., 511 Union Pl.
**Hinckley.**—McKee, Geo. M.
**Ithaca.**—
Bancroft, Dr. W. D., Cornell Univ.
Dennis, Prof. L. M., Cornell Univ.
Mathers, F. C., 217 Mitchell St.
Schluederberg, Carl G., 715 E. Buffalo St.
Snowdon, R. C., 420 Eddy St.
**Kingston.**—Granja, Rafael, Box 799.
**Lansingburgh.**—Valentine, Wm.
**Lockport.**—
Kenan, Wm. R., Jr., 242 Genesee St.
Ruthenburg, Marcus.
**Mechanicville.**—
Griffin, Martin L.
Sadtler, P. B., W. Va. Pulp and Paper Co.
**Monticello.**—Isakovics, Alois von, Synfleur Scientific Laboratories.
**Mt. Vernon.**—Blackmore, H. S., 206 S. 9th Ave.
**New York.**—
Albro, A. B., 510 W. 23d St.
Allyn, R. S., 277 Broadway.
Archbold, De Geo., 101 Franklin St.
Atwood, G. F., Western Elec. Co.
Austen, Dr. Peter T., 89 Pine St.
Bakewell, T. W., 31 Nassau St.
Barstow, W. S., 56-58 Pine St.
Baskerville, Dr. Chas., College City of New York.
Batchelor, Chas., 52 Broadway.

Bijur, Jos., 46 W. 96th St.
Block, Wesley S., 40 Wall St.
Bogue, C. J., 213-215 Centre St.
Bowman, Walker, 39 Cortlandt St.
Bradley, C. S., 44 Broad St.
Breneman, A. A., 97 Water St.
Brown, H. P., 120 Liberty St.
Brown, J. Stanford, 489 5th Ave.
Caldwell, Edw., 114 Liberty St.
Cameron, Walter S., 239 W. 136th St.
Carse, David B., 71 Broadway.
Chandler, Dr. C. F., Columbia Univ.
Clark, Wm. J., 44 Broad St.
Cleaves, Dr. Margaret A., 616 Madison Ave.
Coho, H. B., 26 Cortlandt St.
Crocker, Dr. F. B., 14 W. 45th St.
Devlin, S. B., 156 W. 13th St.
Dodge, Norman, Mergenthaler Linotype Co.
Doremus, Dr. Chas. A., 65 W. 53d St.
Dreyfus, Dr. Wm., 162 E. 95th St.
Duncan, Dr. Louis, 56 Pine St.
Dunn, Clifford E., 13-21 Park Row.
Durant, Edw., 115 E. 26th St.
Eimer, August, 205 3d Ave.
Elliot, Arthur H., 4 Irving Place.
Falding, F. J., 55 Broadway.
FitzGibbon, R., 534 Canal St.
Foregger, Dr. R. von, 100 William St.
Frasch, Hans A., 52 Broadway.
Fries, H. H., Ph.D., 92 Reade St.
Goepel, C. P., 290 Broadway.
Granbery, J. H., 43 Exchange Place.
Hammer, Wm. J., 153 W. 46th St.
Hatzel, J. C., 571 5th Ave.
Havemeyer, H. O., 117 Wall St.
Herzog, F. B., Ph.D., 51 W. 24th St.
Howe, Henry M., Ph.D., 27 W. 73d St.
Howell, Wilson S., 80th St. and East End Ave.
Jackson, H. A., 1 W. 30th St.
Jenks, W. J., 120 Broadway.
Kahn, Julius, 100 W. 80th St.
Kennedy, J. J., 52 Broadway.
Kenyon, Wm. H., 49 Wall St.
Kern, Edw. F., Columbia Univ.
Klipstein, E. C., 122 Pearl St.
Knudson, A. A., 34 Nassau St.
Langton, John, 99 John St.
Lockwood, Chas. E., 439 E. 144th St.
Loeb, Morris, 273 Madison Ave.
Lyndon, Lamar, 80 William St.
Macdonald, Jas. A., 49 Wall St.
Mailloux, C. O., 76 William St.
Matthew, H. T., 114 Liberty St.
Maynard, Geo. W., 20 Nassau St.
McNeill, Ralph, 223 W. 106th St.
Mershon, Ralph D., 116 W. 85th St.
Metz, H. A., 122 Hudson St.
Meyer, Dr. Franz, 52 Broadway.
Monell, A., 43 Exchange Place.
Morehead, J. T., 99 Cedar St.
Morgan, Dr. J. L. R., Columbia Univ.
Nichols, Wm. H., Sc.D., LL.D., 25 Broad St.
Nichols, W. S., 2415 Park Row Bldg.
Pattison, Frank A., Fuller Bldg.
Potter, Henry Noel, Sc.D., 510 W. 23d St.
Prindle, E. J., 220 Broadway.
Pring, John N., 245 Broadway.
Ries. E. E., 116 Nassau St.
Riker, John J., 46 Cedar St.
Roberts, I. L., 60 Wall St.
Roberts, J. C., Broadway.
Roeber, Dr. E. F., 114 Liberty St.
Roller, F W., 203 Broadway.
Rossi, A. J., 35 Broadway.
Ruhl, Louis, P. O. Box 1999.
Rynard, Wm. T., 25 Broad St.
Saxe, Sigmond, 107 Manhattan Ave.
Schuetz, F. F., 132 Nassau St.
Scudder, Heyward, 21 E. 22d St.
Seward, Geo. F., 99 Cedar St.
Speiden, C. C., 181 Front St.
Spice, Robert, Cooper Union for the Advancement of Science and Arts.
Stein, Emanuel, 45 Broadway.
Stutz, E., 43 Exchange Place.
Teeple, Dr. J. E., 164 Front St.
Thatcher, C. J., The Ansonia.
Thelberg, Dr. John, 45 W. 32d St.
Thompson, R. M., 41-43 Wall St.
Toch, Maximilian, 320 5th Ave.
Tucker, Samuel A., Columbia Univ.
Waldo, Leonard, 49 Wall St.
Waterman, F. N., 100 Broadway.
Weaver, W. D., 114 Liberty St.
Wells, G. A., 61 Broadway.
Westmann, G. M., 1144 Broadway.
Wetzler, Jos., 257 W. 104th St.
White, J. G., 43-49 Exchange Place.
White, Ray Hill, 52 Beaver St.
Wichern, Dr. G., 6 Hanover St.
Wigglesworth, Henry, 25 Broad St.
Winship, Dr. Walter E., 1 W. 34th St.
Wittnebel, E. S., 122 Pearl St.
Wolcott, T., 39 Whitehall St.
Wood, E. F., 43 Exchange Place.

**Niagara Falls.—**
Acheson, E. G.
Acker, Chas. E., 104-105 Gluck Bldg.
Acker, O. E., Acker Process Co.
Barton, Philip P., 352 Buffalo Ave.
Becket, Fred. M., Niagara Research Laboratories.
Bennie, P. McN., FitzGerald & Bennie Laboratories.
Benoliel, S. D., Roberts Chem. Co.
Buck, H. W., 123 Buffalo Ave.
Buck, Leon H., Acker Process Co.
Carveth, H. R., Ph.D., 118 Buffalo Ave.
Childs, D. H., Pittsburgh Reduction Co.
Coit, Chas. W., 315 Buffalo Ave.
Collens, C. L., 2d, Can. Niagara Power Co.
Cox, G. E., 315 Buffalo Ave.
Doerflinger, W. F., Acker Process Co.
Earl, W. T., Acker Process Co.
FitzGerald, F. A. J., FitzGerald & Bennie .Laboratories.
Fowler, R. E., The National Electrolytic Co.
Franchot, S. P., Nat. Electrolytic Co.
Giles, I. K., Niagara Electrochem. Co.
Hall, Chas. M., Aluminum Co. of America.
Hall, S. F., Norton Co.
Haskell, F. W., Carborundum Co.
Hedlund, Marten, 362 First St.
Higgins, F. W., The Carborundum Co.
Horry, W. S., Cons. Lake Superior Power Co.
Lathwood, Arthur, Box 238.
LeMare, E. B., 338 First St.
Lidbury, F. A., Oldbury Electro-Chem. Co.
Machalske, F. J., P. O. Box 276.
MacMahon, Jas., Castner Electrolytic Alkali Co.
Marshall, Jas. G., 1115 Niagara St.
Mauran, Max, Castner Electrolytic Alkali Co.

Moritz, C. H., Pittsburgh Reduction Co.
Phillips, Ross, National Electrolytic Co., Bichromate of Soda Plant.
Pretzfeld, Dr. C. J., National Electrolytic Co.
Rodgers, A. G., The Carborundum Co.
Smith, E. S., The Carborundum Co.
Speiden, E. C., Int. Acheson Graphite Co.
Stamps, F. A., P. O. Box 250.
Steere, T. E., Castner Electrolytic Alkali Co.
Tone, F. J., The Carborundum Co.
Vaughn, C. F., Castner Electrolytic Alkali Co.
Zimmerman, C. I., The Carborundum Co.

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**Norwich.**—Stofer, Richard C., 28 Hayes St.
**Ossining.**—Wilder, Stuart, Northern Westchester Lighting Co.
**Owego.**—Govers, Francis X., By-Products Co.
**Peekskill.**—Haug, Arthur, 1710 Main St.
**Penn Yan.**—
Goodwin, Jos. H., 331 N. Main St.
Taylor, E. R.
**Piermont.**—Main, Wm.
**Poughkeepsie.**—Moulton, C. W., Vassar College.
**Prince Bay.**—Johnston, Wm. A.
**Rochester.**—Buckley, Hubert, 431 Lake Ave.
**Schenectady.**—
Beckman, J. W., 223 Union St.
Berg, Ernest J., General Electric Co.
Capp, J. A., General Electric Co.
Creighton, E. E. F., 225 Union St.
Marvin, A. B., Gen. Elec. Co.
Pease, Harold C., Gen. Electric Co.
Steinmetz, C. P., Gen. Electric Co.
Rushmore, D. B., Gen. Electric Co.
Whitney, Dr. W. R., Gen. Electric Co.
**Syracuse.**—
Pennock, J. D., Solvay Process Co.
Sykes, H. W., 206½ Barrett St.
**Troy.**—Betts, Anson G., Head 16th St., N.
**Wardenclyffe, L. I.**—Tesla, N.
**Yonkers.**—
Harrington, Dr. E. I., 87 N. Broadway.
Ihlder, J. D.
McNaier, J. T., "Rockledge."
**Yonkers-on-Hudson.**—Baekeland, L., "Snug Rock," Harmony Park.

## NORTH CAROLINA.

**Chapel Hill.**—Mills, J. E.
**Charlotte.**—Gilchrist, Peter S.

## OHIO.

**Akron.**—
Goodrich, C. C., The B. F. Goodrich Co.
Shaw, E. C., The B. F. Goodrich Co.
Wills, J. M., U. S. Stoneware Co.
**Cincinnati.**—
Hutchinson, E. J., 1245 3d St.
Lowenberg, L., 2229 Park Ave.
**Cleveland.**—
Cowles, A. H., 361, The Arcade.
Crider, J. S., Lock Drawer "L."
Finck, Albert, 92 Streator Ave.
Graves, Walter G., The Grasselli Chem. Co.
Hobbs, Dr. P. L., 347 Erie St.
Koehler, Wm., 1614 Superior St.
Smith, A. W., 1971 E. 79th St., N. E.
Whitlock, E. H., Nat. Carbon Co.
Woodward, J. M., 1228 Citizens' Bldg.
**Dayton.**—Deeds, Edw., Nat. Cash Register Co.
**East Cleveland.**—Baker, Chas. E., 50 Holyoke Ave.
**Elyria.**—Little, C. A., 147 W. Bridge St.
**Lakewood.**—Burwell, Dr. A. W., Kyle Road.
**Salem.**—Davis, D. L., 299 Lincoln Ave.
**Sandusky.**—Curtis, C. C.
**Youngstown**—Klugh, B. G., 886 Mahoning Ave.

## OREGON.

**Eugene.**—Huddle, W. J., Univ. of Ore.
**Portland.**—Cheney, W. C.

## PENNSYLVANIA.

**Altoona.**—Dudley, Dr. C. B., Drawer 156.
**Aspinwall.**—Lodyguine, A., P. O. Box 329.
**Bethlehem.**—
Conlin, Fred., 355 Market St.
Franklin, Prof. W. S., Lehigh Univ.
Landis, W. S., 211 S. New St.
MacNutt, Barry, 841 Seneca St.
Queneau, A. L. J.
Rau, Albert G., Supt. Moravian Parochial School.
Richards, Dr. J. W.
**Bradford.**—Lovejoy, D. R., Bradford Eng. and Mfg. Co.
**Colwyn.**—McConnell, J. Y.
**Dunbar.**—Hamilton, L. P.
**Easton.**—Hart, Dr. Edw., Lafayette College.
**Hokendauqua.**—Thomas, J. W.
**Lansdowne.**—Ernst, C. A.
**Palmerton (Carbon Co.).**—Buch, N. W.
**Philadelphia.**—
Bacon, Ellis W., 3603 Baring St.
Banks, Wm. C., 1037 E. Chelten Ave.
Breed, George, 931 Real Estate Trust Bldg.
Brock, Robert C. H., 1612 Walnut St.
Clamer, G. H., Ajax Metal Co.
Decker, Frank A., 3314 N. 20th St.
Devereux, Washington, 1625 N. 29th St.
Divine, Wm. P., 2102 Tioga St.
Eglin, W. C. L., 235 S. 42d St.
Ely, T. N., P. R. R. Co.
Fahrig, Ernest, 1017-18 Betz Bldg.
Fraley, J. C., 1815 The Land Title Bldg.
Hance, A. M., Hance Bros. & White.
Harris, W. D., 3609 Ludlow St.
Hering, Carl, 929 Chestnut St.
Hitchcock, Fanny R. M., 4038 Walnut St.
Howard, Geo. M., 19th and Allegheny Ave.
Hunter, T. G., 630 Real Estate Trust Bldg.
Kitsee, Dr. Isador, 306 Stock Exchange Place.
Lafore, J. A., 119 S. 11th St.
Meyer, John, 5345 Pine St.
Moltkehansen, I. J., Harrison Bros., Inc.
Morris, Henry G., 333 Walnut St.
Oliver, F. M., H. K. Mulford Co.
Paramore, E. C., 111 Queen St., Gtn.
Paul, Henry N., Land Title Bldg.

Perry, R. S., 5104 Pulaski Ave., Gtn.
Reed, C. J., 3313 N. 16th St.
Rodgers, Wm. J., 516 Arch St.
Roepper, C. W., Mt. Airy Station.
Rowland, A. J., 4510 Osage Ave.
Russell, C. J., 4522 Frankford Ave.
Sadtler, Dr. S. P., 39 S. 10th St.
Sadtler, S. S., 39 S. 10th St.
Salom, Pedro G., 333 Walnut St.
Scholl, Dr. G. P., 929 Chestnut St.
Shinn, A. J., 1224 N. 12th St.
Smith, Dr. Edgar F., Univ. of Pa.
Smith, E. W., 74 E. Penn St., Gtn.
Smith, Wm., 6942 Marsden St., Tacony.
Steinmetz, J. A., 401 Market St.
Taggart, Walter T., 717 Corinthian Ave.
Wahl, Dr. W. H., Franklin Inst.
Wilbert, M. I., German Hospital.
Williams, H. J., 5019 Franklin St., Frankford.
Zeller, Edwin A., Jr., Lock Box 1630.

**Pittsburgh.**—
Armor, Jas. C., 931 Vickroy St.
Barrett, Jas. M., Phipps Power Bldg.
Flanders, L. H., Westinghouse M. Co.
Greenstreet, C. J., Pittsburgh Plate Glass Co.
Isaacs, A. S., 404 Smithfield St.
James, Dr. J. H., Carnegie Tech. School.
Lease, L. J., 159 Flavel St.
Lincoln, P. M., 6830 Thomas St.
Merrill, J. L., 1526-30 Park Bldg.
Osborne, L. A., W. E. & Mfg. Co.
Rodman, Hugh, Westinghouse Machine Co.
Slocum, F. L., 401 S. Linden Ave., E. E.

**Primos.**—
Boericke, Gideon, Primos Chem. Co.
Stein, W. M., Primos Chem. Co.

**Scranton.**—Stock, H. H., Mines and Minerals.

**State College.**—
Myers, Prof. Ralph E.
Pond, G. G.

**Tarentum.**—Hitchcock, H. K.

**Uniontown (Fayette Co.).**—Baum, I.

### RHODE ISLAND.

**Providence.**—
Catlin, Chas. A., 133 Hope St.
Perry, C. M., 4 Catalpa Road.

### SOUTH DAKOTA.

**Clemson College.**—Doggett, C. S.

### TENNESSEE.

**Chattanooga.**—Thomas, B. F.

**Nashville.**—Dudley, Prof. Wm. L., Vanderbilt Univ.

### TEXAS.

**Austin.**—
Harper, Dr. H. W., Univ. of Texas.
Phillips, Wm. B., Univ. Station.
Schoch, Dr. E. P., 714 W. 23d St.

**Beaumont.**—MacFadden, C. K.

**Fort Worth.**—Boon, Prof. J. D., Polytechnic College.

### UTAH.

**Bingham Canyon.**—Cates, Louis S., Boston Cons. Min. Co.
Bennett, E., Telluride Power Co.

**Provo City.**—Smith, Frank Warren.

**Salt Lake City.**—Merrill, Prof. J. F., Univ. of Utah.
Prosser, H. A., 508 Dooly Block.

### VERMONT.

**Burlington.**—
Boynton, Dr. C. S., 69 N. Prospect St.
Freedman, Prof. W. H., 100 S. Union St.

### VIRGINIA.

**Holcomb's Rock.**—
Kugelgen, F. von., The Va. Electrolytic Co.
Lee, H. R.
Seward, George O., The Va. Electrolytic Co.

### WASHINGTON.

**Tacoma.**—Jones, L. J. W., Tacoma Smelting Co.

### WEST VIRGINIA.

**Clarksburg.**—Chorpening, Geo. B.

**Morgantown.**—
Hite, B. H., W. Va. Experiment Station, Ltd.
Wadsworth, F. L. O., Pressed Prism Plate Glass Co.

### WISCONSIN.

**Madison.**—
Beebe, Murray C., Univ. of Wis.
Burgess, C. F., Univ. of Wisconsin.
Eggers, H. E., 812 W. Johnson St.
Engle, Simon G., 127 W. Gilman St.
Hanks, M. W., 216 Langdon St.
Jackson, Prof. D. C., Univ. of Wis.
Johnson, A. R., 308 Mills St.
Kahlenberg, Dr. L., 234 Lathrop St.
Kowalke, O. L., 430 Francis St.
Shinn, F. L., 1216 Spring St.
Watts, O. P., 313 Johnson Court.

**Milwaukee.**—
Hutchinson, R. W., Jr., Nat. Brake and Elec. Co.
Pinkerton, A., 1015 Railway Exchange.
Rogers, A. J., 318 Ogden Ave.
Vogel, G. C., Pfister & Vogel.
Zimmerman, J. G., 622 Otjen St.

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## AFRICA.

### CAPE COLONY.

**Somerset West.**—Quinan, Kenneth B., Dynamite Factory.

### ALBERTA.

**Frank.**—Arnold, T. Herbert, The Pass Power and Lighting Co.

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## AUSTRIA.

**Vienna.**—Paweck, Dr. H., Dittesgasse, 16.

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## BELGIUM.

**Brussels.**—Solvay, A., 33 Rue du Prince Albert.

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## BRAZIL.

### MINAS GERAES.

**Morro Velho.**—Wilder, F. L., Villa Nova de Lima.

## CANADA.

### BRITISH COLUMBIA.

**Grand Forks.**—Bishop, Walter M.
**Nelson.**—Fowler, S. S., P. O. Drawer 1024.

### NEWFOUNDLAND.

**St. Johns.**—Harvey, E. F.

### ONTARIO.

**Cobalt.**—Evans, J. W.
**Copper Cliff.**—Browne, David H., Can. Copper Co.
**Kingston.**—Goodwin, Prof. W. L.
**Ottawa.**—Haff, Max M., 188 Metcalfe St.
**Sault Ste. Marie.**—
Rhodin, B. E. F., Canadian Electro-Chem. Co.
Sjostedt, E. A., Lake Superior Power Co.
**Toronto.**—
Lewis, Henry F., 1103 Temple Bldg.
Miller, W. L., 50 St. Albans St.
Rosebrugh, Prof. T. R., School of Practical Science.
Van Winckel, W. H., 148 Van Horne St.
Wells, J. Walter, 392 Markham St.

### QUEBEC.

**Buckingham.**—Gibbs, W. T., The Electric Reduction Co., Ltd.
**Montreal.**—
Barnes, H. T., D.Sc., McGill Univ.
Brandeis, Chas., 160 St. James St.
Herdt, Prof. L. A., McGill Univ.
McIntosh, D., McGill University.
Stansfield, Prof. A., McGill Univ.
**Shawenegan Falls.**—Witherspoon, R. A., Shawenegan Carbide Co., Ltd.

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## CUBA.

**Ensenada de Mora.**—Roush, G. A.

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## ENGLAND.

**Birmingham.**—Threlfall, Richard, 30 George Road.
**Liverpool.**—Smith, A. T., 43 Castle St.
**London.**—
Ashcroft, E. A., 82 Victoria St., S. W.
Cowper-Coles, S., Grosvenor Mansions, Victoria St.
Perkin, Dr. F. M., 103 Borough Road.
Shields, Dr. J., 4 Stanley Gardens, Cricklewood.
**Manchester.**—Hutton, R. S., The University.
**Merton.**—Stevens, T. B., "Hazelmere," Devonshire Road, Collier's Wood, S. W.
**Newcastle-upon-Tyne.**—
Ewing, A. J., 158 Rye Hill.
Leathart, Jas. G., Locke Blackett & Co., Ltd.
Merz, Chas. H., Collingswood Bldgs.
**Sheffield.**—Hadfield, R. A., Parkhead House.
**Stafford.**—Vicarey, R. W., 91 Foregate St.

## FRANCE.

**La Praz.**—Heroult, Dr. P. L. T.
**Nancy.**—Arth, G., Rue Grandville I.
**Paris.**—
Combes, C., 29 Avenue Rapp.
Drake, Francis E., 45 Rue de'l Arcade.
Garfield, A. S., 67 Ave. de Malakoff XVI. Arrond.
Gin, G., 43 Rue de Levis (VIIe).
Marie Marie, Charles A., 98 Rue du Cherche Midi.
**Versailles.**—Gall, Henry, 5 Rue Albert Joly.

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## GERMANY.

**Charlottenburg.**—Engelhardt, V., Schlossstrasse 11, 2.
**Essen-Ruhr.**—Goldschmidt.
**Frankfurt a|M.**—
Glenck, I. A. H.
de Neufville, Dr. R., Junghofstrasse 14.
**Hanau.**—Heraeus, Heinrich.
**Hocht, a|M.**—Reisenegger, Dr. H., Farbwerke.
**Karlsruhe.**—Habel, Prof. Dr. F., Technische Hochschule.
**Leipzig.**—
Le Blanc, Prof. Dr. M., Physikalisch-Technisches, Institut der Universitat.
Wagner, Dr. J., Mozart Strasse 27.
**Nurnberg.**—Askenasy, Dr. Paul, Jagdstr. 12.

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## HAWAIIAN ISLANDS.

**Honolulu.**—Shorey, E. C., P. O. Box 360.

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## INDIA.

**Bangalore.**—Gibbs, H. P.
**Sivasamudram.**—Hobble, A. C.

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## ITALY.

**Rome.**—
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Paterno, Prof. Emanuel, via Panisperna.

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## JAPAN.

**Kure.**—Tada, S., Kure Naval Arsenal.
**Kyoto.**—Namba, Prof. M., Univ. of Kyoto.
**Osaka.**—Fukuda, M., 18 Watayamachi-Kitaku.
**Tokyo.**—
Brindley, G. F., 3 Itchome, Uchisaiwai Cho, Kojimachi-Ku.
Nakayama, Takakichi, Fugi Paper Co., Sanjikkenbori.
Masujima, B., K. Takebe, 25 Gazenbo-Cho, Azabukn.
Shinjo, Y., 78 Miyamuracho, Azabn.
Tada, Shigekane, 1st Section of Kwanseihonbu, Navy Dept.
**Yokohama.**—Sakai, S., Yokohama Gas Works.

157533



### MEXICO.

**Aguascalientes.**—Garduno, Jesus.
**Cananea.**—Guess, G. A., Cananea Con. Copper Co.
**Dinamito (Durango).**—Chiaraviglio, Ing. Dino, Compania National Mexicana, de Dinamito y Explosivos.
**El Oro (Estado de Mexico).**—Herrera, Benito, c|o Hotel de Jardin.
**Guadalajara.**—Jackson, Chas., Apartado No. 27.
**Torreon (Coahuila).**—Haas, Herbert, c|o Cia Met. de Torreon S. A.
**Villa Corrono.**—Carnaghan, E. D.

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### NORWAY.

**Vadeim (Sogn).**—Moltkehansen, I. J.

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### PERU.

**Cerro de Pasco.**—Taylor, J. F., Cerro de Pasco Mining Co.

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### RUSSIA.

**Kharkov.**—Piltschikoff, Prof. Nicholas, Technological Inst.

### SCOTLAND.

**Edinburgh.**—Irvine, H. A., 51 Fountainhall Road.
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### SWEDEN.

**Alby.**—Petersson, Dr. Albert.
**Mansbo (Avesta).**—Carlson, Birger.
**Stockholm.**—Kjellin, F. A., Sturegatan 56.
**Vesteras.**—Edstrom, J. Sigfrid.
**Westervik.**—Tillberg, E. W.

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### SWITZERLAND.

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Lacroix, Henry, Usine de Degrossissage d'or.
**Turgi.**—Landolt, Dr. Hans.
**Zürich.**—
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*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

# FORMULA FOR THE HELMHOLTZ CONCENTRATION CELL.

By Henry S. Carhart, LL.D.

In my paper on "A Thermo-electric Theory of Concentration Cells"[1], I maintained the theorem that *"concentration cells are devices for converting heat from their surroundings into electrical energy."* The well-known equation of Helmholtz for the electromotive force of any voltaic cell is

$$E = \frac{H}{Q} + T\frac{dE}{dT},$$

in which $H$ is the heat equivalent of the chemical reactions in the cell. The second term of this expression is dependent on the temperature coefficient of the cell $dE/dT$, and this coefficient is now admitted to be due to the thermo-electromotive force at the several junctions of dissimilar substances in the cell. Whenever, therefore, the conditions are such that the heat of reaction and of dilution is negligible, the first term becomes zero and only the second, $T\frac{dE}{dT}$, remains. Such are very approximately the conditions in a simple Helmholtz concentration cell, in which two electrodes of the same metal are immersed in solutions of a salt of that metal, the concentration of the solution being different at the two electrodes. The E. M. F. of such a cell is thermo-electric in origin and should be represented by the second term of the Helmholtz equation.

The same conclusion may be reached in another way. In my paper, above referred to, may be found a curve (Fig. 4, page 126) expressing the relation between thermo-electromotive forces per degree C. and the corresponding concentrations for Zn —

[1] Trans. Amer. Electrochemical Soc., Vol. II. p. 123.

$ZnSO_4$. From this curve the following equation may be derived in terms of the absolute temperature and the concentration:

$$dE = a \cdot T \frac{dC}{C} .$$

Whence by integration $E = a \cdot T \log C$.

*T* is the absolute temperature, *a* is a constant and *C* is the concentration. *E* is here the potential difference at a single electrode For two electrodes immersed in solutions differing in concentration, the E. M. F. is the difference between two such expressions, or

$$E = a \cdot T \log C_2 - a \cdot T \log C_1 .$$

This reduces immediately to

$$E = a \cdot T \log \frac{C_2}{C_1} .$$

This equation will be recognized as the simplest form of the Nernst expression for the E. M. F. of such a cell. Nernst derived it from the theory of osmotic pressure.

The derivative of *E* with respect to *T*, found by differentiating the above equation, is

$$\frac{dE}{dT} = a \cdot \log \frac{C_2}{C_1} .$$

Solve for the constant *a*, substitute its value in the equation for *E*, and we get

$$E = T \frac{dE}{dT} ,$$

the second term of the Helmholtz equation.

We have thus the connection between the Helmholtz and the Nernst equations, and at the same time it appears that the latter may be derived entirely from thermo-electric data. Also, both equations lead to the same conclusion, namely, that the E. M. F. of a simple Helmholtz concentration cell is numerically equal to the expression, $T \frac{dE}{dT}$ .

A concentration cell with pure silver electrodes and solutions

of silver nitrate, whose concentration ratio was 5.26, gave an E. M. F. at 30° C. of 0.0452. The mean of two determinations of the temperature coefficient, dE/dT, was 0.000144. Whence *E*, calculated by the expression $T \frac{dE}{dT}$, is

$$E = 0.000144 \times 303 = 0.0436.$$

A similar concentration cell with cadmium amalgam and one-tenth and one-hundredth normal cadmium sulphate solutions had an E. M. F. at 22.35° C. of 0.034 volt. The mean temperature coefficient was 0.0001085. Whence

$$E = 295.35 \times 0.0001085 = 0.032.$$

In both cases the calculated values are quantities of the same order as the observed values.

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## DISCUSSION.

PRESIDENT HERING: There is a point that appeals to me in the paper, namely, the portion in italics in the very beginning. The author says, "I maintain the theorem that the concentration cells are devices for converting heat from their surroundings into electrical energy." Now, if that statement were true, it seems to me it contradicts the second law of thermodynamics, because it would be a means for converting the low grade heat of the surroundings into the high order of energy of an electric current.

DR. BANCROFT: May I call attention to the other alternative, and that is that those cells will not go on indefinitely and that consequently there is not any contradiction so far as I can see. You start with a cell which contains two different concentrations. The cell keeps going until it is run down and then the whole thing comes to an end; personally that does not strike me as being in conflict with the second law of dynamics.

PRESIDENT HERING: Ought not this statement in the paper be modified, in that case? The statement gives the impression that

those cells convert the heat of the surrounding air into electrical energy. Now, if something else takes place also, it ought to be included in that statement.

Dr. Bancroft: I assume that Mr. Carhart intends all the other things to be covered by the explicit reference to concentration cells.

Personally I have another comment to make on the paper, and that is that this connection between the Helmholtz and the Nernst equation was pointed out in 1899.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, Mr. C. E. Acker in the chair.*

# VISIBLE MIGRATION OF PARTICLES BETWEEN ELECTRODES.

By Carl Hering.

In the electrolytic deposition of iron, it has been stated that the deposited iron sometimes contains carbon from the cast iron or steel anode. As the solution used does not chemically dissolve carbon, it follows that the carbon could not have passed from the anode to the cathode by the process of electrolysis. An explanation of its transfer is, therefore, due.

In another instance, it was reported by our past president, Dr. Bancroft, that in the electrolytic deposition of alloys, he found the deposit on the cathode contained some oxide. But one of the useful laws of electrolysis, though perhaps one which is not as generally known and accepted as it should be,—is that in electrolysis the chemical process at the cathode is always a reduction, and at the anode is always an oxidation (or better a *perduction* as suggested by Prof. Richards). If this very useful law is correct, it would be an electrochemical impossibility for an oxide of the deposited metal to be formed electrolytically at the cathode from the metal of the anode. Hence an explanation of its appearance at the cathode is desired.

In still another instance, it has been reported that sometimes the deposit of silver in a silver voltameter exceeded that required by Faraday's law. Assuming that it was not due to some error, an explanation is called for.

Still another instance might be cited here, namely that when a bath is turbid with suspended particles, the deposits on the cathode are said to become rough, due to the foreign particles becoming enmeshed by the molecules of the metal which is being deposited. But it is difficult to conceive how such particles, which are not ions, could approach to within a molecular distance of the cathode, and if they do not, how could the molecular deposits

ever surround these enormously larger particles. When muddy water freezes slowly, the resulting ice is clear.

The above cases are cited here as an indication that particles which are mechanically suspended in an electrolyte, and, therefore, not subject to electrolytic action, may perhaps be subject to some other electrical action, and if so it might explain the results obtained.

During the past winter, Dr. Edwin F. Northrop and the writer made some microscopic researches in connection with the very interesting, curious, and still unexplained Brownian movements, those persistent and untiring movements of minute, lifeless bodies which are perhaps still the closest approach to an apparent perpetual motion yet observed. These small but molar particles (which for convenience of reference we nicknamed "brownies") were subjected by us to the influence of an electric current in the surrounding liquid, or to charged electrodes in insulating liquids and we then noticed that they wandered across the field from one electrode to the other. Their motion was very decided; it was along the lines joining the electrodes, that is, from one electrode to the other, showing that they were attracted by one or the other electrode. Their direction of motion depended upon circumstances; most of them traveled *with* the current, while some traveled in the opposite direction, namely toward the anode; but each particle had its characteristic direction of motion, relatively to the current, which is never changed, at least so far as our experiments showed; in some mixtures of particles of two different materials, those of the one kind traveled with the current and those of the other, against it; when the current was stopped or reversed, their direction of motion was stopped or reversed with great promptness, like an aperiodic galvanometer; they acted as though they had no inertia, that is, as though the moving forces were immensely greater than those due to their inertia. They obeyed the current as promptly as a body of well trained soldiers obey their officer. Their speed increased with the current or the difference of potential between the electrodes, and seemed to be approximately constant for constant electrical conditions; it was under certain conditions so great that the particles raced across the field in a few seconds; the smaller particles, as a rule, traveled faster that the larger ones. In some cases an

extremely small current or difference of potential suffices to move them. These motions were so positively related to the electrical conditions that it suggested the idea to Dr. Northrop of making it the basis of a sensitive electrical measuring instrument for special purposes. A peculiarity of these particles while thus in motion, was that they repelled each other during their migrations; they rarely if ever quite touched each other; when two particles traveling in opposite directions approached each other, they deviated their paths as they passed each other, like two wagons meeting on a narrow road. They acted as though each were surrounded by an invisible sphere of some repellant force like a very elastic jelly. When electrodes were used in non-electrolytes, the particles traveled up to their respective electrodes, and crowded together around them, like floes of ice in a running river, but aparently not quite touching them. The motion took place in electrolytes as well as in insulating liquids; it is not limited to solid particles but takes place also with liquid particles suspended in a non-miscible liquid, like the little spheres of liquid fat in milk; milk, under certain conditions, even shows the rather rare phenomenon of two kinds of particles traveling in opposite directions in the same liquid. Almost all the particles which we examined traveled in the same direction as the current, namely, from the anode to cathode.

The above observations are given here briefly as a visual demonstration of the fact that insoluble molar particles, suspended in a liquid, will have a very definite and decided motion from one electrode to the other, quite similar in some respects to the migrations of the ions of an electrolyte; and that these motions are purely molar, as distinguished from the atomic motions due to the chemical interchange of atoms assumed in the usual explanation of the phenomenon of electrolytic migration. It has been known that some colloids travel bodily when a current is passed through them, and as many of the colloids show Brownian movements, the phenomenon above described may be of the same nature, and, if so, it is not new, but, perhaps, the visual demonstration in the microscope is new, or at least of interest.

This phenomenon of the non-electrolytic bodily transfer of molar particles by the current, is offered here by the author as a possible explanation of the observation of certain facts in elec-

trolysis like those stated at the beginning of this paper. For instance, the particles of carbon noticed in electrolytic iron may have been carried over from the anode by this molar migration. The metallic oxide found on the cathode may thus have been carried over bodily from the anode as an insoluble particle of oxide. The excess of weight in the silver voltameter may have been due to such molar particles migrating over from the anode. The effect of the turbidity of solutions on the nature of the cathodic deposit, may be due to the fact that these molar particles were thus moved by the current, generally toward the cathode. The particles appear to have some electrical property like a charge, and hence may have a tendency to take some part in the electrolytic phenomenon of the deposition of the ions on the cathode by which they are surrounded and enclosed, thereby becoming apparently a part of the deposite. For the avoidance of this molar transfer of matter, a porous partition naturally suggests itself, but its pores must be smaller than these extremely small particles, (about one micron).

As an explanation of the cause of this migration, it was suggested that the phenomenon might be the same as the well known movement of a globule of mercury in sulphuric acid between two electrodes, in which the motion has been explained to be due to the differences of surface tensions produced by the current on the two sides of the globule. We, therefore, made an experiment in which the mercury was replaced by a solid conducting body floated between two liquids of different densities; but although it was much lighter than the globule of mercury, it showed no signs of any movement, while the mercury moved very decidedly. In another experiment this solid conducting body was replaced by a globule of an insulating liquid, but again there was no motion, although this globule was much smaller and lighter than the mercury. Moreover, in some of our microscopic experiments, the particles moved when placed in insulating liquids. In view of all these facts it seems that this phenomenon of the moving particles is not the same as that of the globule of mercury, and that a different explanation must, therefore, be looked for.

## DISCUSSION.

Dr. W. D. Bancroft: It seems to me that what Mr. Hering has watched in the microscope is the reverse of electrical endosmose. If you have a porous diaphragm which is fixed, then the solution flows through it when under electrical stress. If the diaphragm is disintegrated, it flows through the liquid in the reverse direction. The general theory was pretty fairly well covered by Quincke. If these particles are all charged, positively or all negatively, they would not coalesce. They would travel through the solution exactly as Mr. Hering describes.

I am not quite in sympathy with the reasons for which the investigation was begun. While all things are possible, and therefore metallic oxide may be carried from the anode to the cathode, it doubtless is not the explanation of the appearance of oxide on the cathode when you work under unsuitable conditions. In one particular case, in a copper sulphate solution, the oxide comes from the decomposition of cuprous sulphate by water. I don't see why oxides should not be formed in a manner similar to the formation of caustic soda at the cathode. In some solutions it is very difficult to prevent the formation of oxides; but the theory of the phenomenon is simple.

Mr. Carl Hering: Endosmose was of course considered by us as a possible explanation, but it does not explain why some particles move in one direction and some in the other, when the glass plates are considered the diaphragm, and the moving liquid is assumed to carry the brownies bodily with it. If the motion of those particles was due to endosmose between the glass plates they would all move in one direction, namely the direction in which the liquid moved. Among other experiments we made the following observation: We put an insulating liquid between two thin, gold-leaf electrodes, added some brownies and covered it with a cover glass. We then applied the poles of a battery to the electrodes and found that some of the brownies traveled one way, and some the other, although, of course, there was no current flowing. After a while the field became nearly clear and we then moved the slide so as to show one of the electrodes, when we found all the particles of one kind clustered around that electrode; the others were clustered around the other. When we reversed the current

while watching this electrode, they all bodily moved off from the electrode in a bunch, just like floes of ice in a river when the current is suddenly changed so as to flow from the shore. They did not start off one after the other, but they all started together like a lot of soldiers. They kept together, and moved at about the same velocity.

The reason for making these investigations was not to explain the phenomena mentioned in the beginning of the paper, as Prof. Bancroft has assumed. They were made to study the Brownian movements, and it was only incidentally that I thought some of those observations might explain some electrical effects which have, in my opinion, not yet been explained.

Prof. Bancroft does not explain the appearance of carbon in iron. Of course, an oxide may be formed on the cathode by some local action, and that may be, and undoubtedly is, the explanation in some cases; but after observing those movements I feel quite sure that particles of oxide may be transferred by the current to the cathode in accordance with the observations we made, and in accordance with the laws which govern those movements.

Dr. Bancroft: It seems as though Mr. Hering and I had different views in regard to the fact concerning electrical endosmose. My understanding of the matter is that if you take one kind of a diaphragm you get the liquid passing through the diaphragm in one direction; if you take a diaphragm of another kind you get the liquid passing in the opposite direction. If you take these two kinds of diaphragms, and grind them up, one set of particles will move one way and the other set the other way. Mr. Hering's experiment shows that when you have two different kinds of particles they may in certain cases move in different directions, precisely in accordance with the facts which are on record.

Mr. C. E. Acker: Last week a patent was issued which may be of interest in this discussion.

Mr. Hering: I intended to mention that interesting patent myself, and in fact I have brought a copy of it with me. In this process the inventor makes use of the very thing which we observed. He makes use of it in this way: he wants to get a smooth electrolytic deposit. He says a rough deposit is caused by the fact that a little crystal starts on the cathode, and as the current density then becomes very great around the crystal, it grows

very rapidly. We know that that is the case. He therefore adds to his solution a lot of those particles, but only of the kind that travel toward the cathode. Then, he says, if a crystal should start to form on the cathode, the current density will become higher there, and those particles will therefore cluster around it in great numbers, forming a diaphragm and introducing resistance in the circuit at that point which then causes less current to go through there and more current to go to the rest of the plate.

It appealed me as being a very ingenious application of this principle of the moving particles. In this patent he also speaks of the fact that some of the particles move to the anode and some to the cathode.

Dr. C. J. Thatcher: I think possibly some light might be thrown on the subject by a study of the effect of porous diaphragms on the particles.

Mr. E. A. Sperry: I would like to ask wherein those particles differ from the particles that interfere with the smooth deposit on the cathode in the case of lead. If there is a particle in the electrolyte and that particle finally rests on the cathode, it usually forms the basis of a wart or excrescence. I noticed in the Betts cathodes, recently examined, the little warts or excrescences, the things that prevent that cathode from being a plane surface, have for their basis a minute particle, often a very fine point and then enlarges so that they can be easily broken off, revealing a little minute particle in there which seems to be the basis of the formation.

If a particle in one case makes a cathode a plane surface and in another case prevents it from being a plain surface, what is the difference in the particle? What is the point in the German patent? Does he confine himself to a certain kind of cathode, electrolyte, etc.?

Mr. Hering: The point Mr. Sperry makes is well taken. This patentee uses seed mucilage, albumen and materials of that sort which are not likely to adhere to or to become enmeshed by the particles on the cathode. The particles I had reference to were more like solid particles, such, for instance, as carbon. A particle of carbon, being a conductor, might well attach itself to the cathode and become the origin of one of those growths. I have always held the opinion that those growths were originated

in just such a way. When a growth is once started it naturally grows very rapidly. Does that answer your question, Mr. Sperry?

Mr. Sperry: Yes, I think it does; but it raises another one. What is the difference between that and the gelatine Betts has used for some time?

Dr. Bancroft: The difference is just this. Mr. Betts uses gelatine because he finds it is effective. In this patent they select things that move to the cathode and which are therefore effective. The question is why does the addition of gelatine or glue or things of that sort produce satisfactory results? On working this out it was shown in the case of copper sulphate that gelatine gives a bright deposit in some cases and not in others. It was next found that when gelatine gave a bright deposit it moved to the cathode, while in the other solutions it moved to the anode. In other words, the essential difference between the behavior of the gelatine and of the rough particles is that the gelatine prevents the crystallization of the metals and causes them to come down in a much finer form, and therefore does not give any point from which a tree can start.

In the case of a solid, non-conducting particle you have a lump on the surface of the cathode and the metal gradually grows around it. I think that is a distinction anyhow between the two. This patent is based solely on the use of gelatine by Betts and others.

Prof. S. A. Tucker: I was wondering if there is any connection between this and a recent patent for bright zinc deposits by the use of certain additions of organic compounds to the bath.

Mr. Hering: In closing this discussion, I desire to say that Prof. Bancroft and I misunderstood each other in the early part of this discussion. In discussing the question of whether this phenomena of the moving particles was or was not explained by endosmose, Dr. Northrup and I assumed the glass slide to be the diaphragm and the film of liquid to be that in one of its pores, the particles being carried bodily by the moving liquid. Prof. Bancroft, however, as I now understand him, assumes the moving particles to correspond to the diaphragm; this explains our apparent disagreement.

Nevertheless it does not seem to me that his explanation is cor-

rect, at least its correctness is not as self-evident and obvious as he assumes. One reason is that we also found these same phenomena with *insulating* liquids between charged electrodes; there could, therefore, have been no current flowing and therefore no such endosmotic action as that due to flowing currents. Another reason is that in endosmose the liquid in most cases* flows *with* the current, and therefore, according to Prof. Bancroft's views, the floating particles should in most cases move *against* the current. We tried a large number of different particles and, with but few exceptions, they all moved *with* the current, and therefore in the opposite direction to that which they should have if the explanation which Prof. Bancroft assumes to be self-evident, were the correct one.

When electrolytes are used instead of insulating liquids, the two glass plates ought to act as a diaphragm with a single pore, and when a current flows it ought to cause the liquid to flow, and generally in the same direction as the current; hence the suspended particles would be carried with it bodily. If in that case a particle moves in the opposite direction, it would indicate that it moves against the liquid and faster than the liquid does.

It seems to me that further research is necessary to determine whether the true explanation of the phenomenon is endosmose or not; but whatever the explanation may be, the observed facts stated in the paper remain the same; and these facts would explain the irregularities sometimes noticed on cathodes, as stated in the paper.

* Whetham, Theory of Solution, p. 292.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

# SOME SMALL LABORATORY APPLIANCES FOR ELECTRIC FUSION AND OTHER WORK.

By S. S. Sadtler.

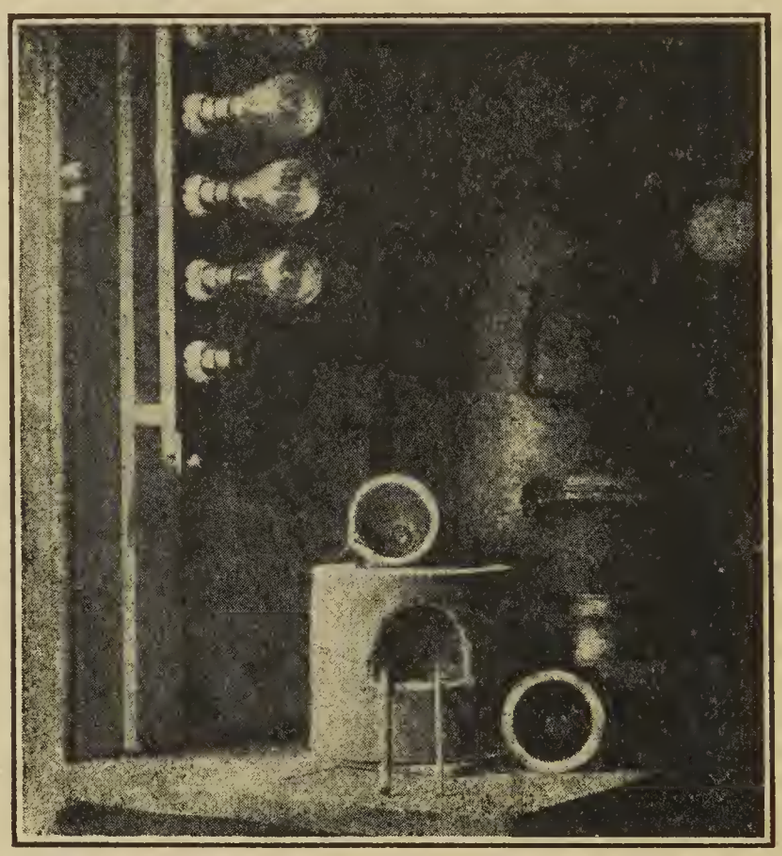
The writer thought of submitting a few notes on the subject of some simple laboratory devices for doing electric fusion work, believing that there are a number of chemists especially who are not regularly equipped for extensive electrochemical work, nor would they contemplate doing so unless certain experiments they had in view showed encouraging initial results.

The writer has used apparatus ordinarily found in a chemical laboratory, for doing quite a range of electrochemical work, and, in a number of cases, when he had exhausted his laboratory facilities, larger furnaces, etc., were installed on terra firma.

The current used for different experiments to be referred to was from the city lighting service, and was of 220 volts, with three wires, the wiring being so arranged that it was practically 110 volts current, although 220 volts could be obtained from the outside wires with very little trouble. A very simple bank of lamps was used to vary the current. Six stationary sockets were fixed to a board and wired in multiple, with binding posts at one end for connection to the work. The current could thus be carried by putting in more lamps, and varying the capacity of the same from 1-5 ampere to 5 amperes, the 1-5 ampere being approximately obtained with the use of one 220-volt, 16-candle-power lamp, while the 5 amperes were obtained by the use of six 110-volt, 32-candle-power lamps, which gave nearer to 5½ amperes. In this way all the current desired was quickly obtainable, and without danger of short circuiting.

For carrying out a quick experiment to see whether a metal is deposited, or to get a rough idea of the state of fluidity of a proposed bath, a Chaddock gas burner is found serviceable, upon

the top of which a small Hessian crucible, or one of iron or nickel can be rested, in which the molten electrolyte can be contained, and the anode, a rod of graphite or whatever is desired, can be dipped into it from a clamp which makes electrical contact, and for a cathode, a very simple and effective device is made as follows: A wire is bent into a spiral at one end, which fits in the bottom of the crucible and more or less covered by the separated metal, and the surface of the wire contained in this spiral is made proportional to the desired current density. The stem of the spiral comes up the inside of the crucible, and is cemented



to it by a plastic mass, which, in some cases, could be fire clay or carborundum powder and silicate of soda, which works satisfactorily for many fusions of a neutral or acid character.

When a larger experiment is to be performed, a Buffalo dental furnace with a large gas blast lamp or gasoline lamp for purposes of heating, is found very satisfactory. In the top of this the crucible can be inserted of proper size, with the same spiral arrangement for cathode. In some cases, where an iron cathode is wanted of considerable surface, a large iron crucible or body of an iron still of about a quart capacity may be used in the furnace.

In some experiments carried out by the author, in which certain gases were passed over a solid at definite temperatures, a tube furnace was employed, which was very effective for the purpose.

In looking up the proper size of platinum wire for electrical heating, it was almost impossible to decide upon the size and amount of wire that would be required, and it was not until a trial was made, that a fair idea could be gotten. The writer thought, therefore, that it would be well to give a few specifications for this furnace, that would enable others to readily make such a simple device.

The tube consisted of Royal Berlin porcelain, of about ½-inch inside diameter, and 2 feet long. Around this, allowing at least 8 inches free at each end, was wrapped platinum wire of No. 28 gauge. It took 10 feet of wire to cover the body of the tube, allowing about ⅛ to 3-16 inch space between the folds of the wire. As the platinum wire was wrapped tight and clamped at the ends with heavy copper wire, the free ends of which were used as electrical terminals, it was not found necessary to put in any insulating material to keep the wire apart. Asbestos cord could have been used for this purpose.

A small section of 3-inch galvanized piping, such as that used for rain spouts, was used for the outside shell, and between this and the tube, a mixture of magnesia and asbestos was packed, sheet asbestos being put on the ends and fastened thereto with silicate of soda and wired.

A variety of rheostats could be used for varying the current. The writer, however, used one of small disks of carbon, the resistance of which was varied by means of a screw. Temperatures varying from 600 or 700°F., to 2000, were used by the writer, and undoubtedly considerably more could have been obtained. The pyrometer used, however, only registered to 2000.

The control of the temperature was gotten by the use of an ammeter in circuit, and a pyrometer, the fire end of which was encased in a small porcelain tube that ran in the larger one and held at one end firmly in place by means of a rubber stopper. The use of an ammeter is quite essential to the successful control of an experiment, as the pyrometer, especially one encased in a porcelain tube, does not register a change in temperature quick enough, and

too high or too low temperatures would be the result where more time would be desirable.

The writer hopes that these notes may be of service to those who may want to undertake some experiments on a small scale.

*Philadelphia, Pa.*

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

## COPPER CATHODES IN NITRIC ACID.

By J. W. Turrentine.

It is known that nitric acid in dilute solutions undergoes reduction, quantitatively, at the cathode. This method is recommended for the quantitative determination of nitrates. This reduction is equivalent, of course, to an action by nascent hydrogen, liberated at the cathode, on the nitric acid, according to the equation:

$$8H_2 + 2HNO_3 = 2NH_3 + 6H_2O.$$

Nitric acid in acting on copper, on the other hand, is reduced not to $NH_3$ but to nitric oxide, as indicated by a free evolution of brown fumes. In other words, copper reduces $HNO_3$ to NO and not to $NH_3$. It reduces nitrobenzene to aniline. Why does it not reduce $HNO_3$ completely? Why does the reduction stop at nitrites?

It was the object of this bit of work to answer these questions.

Since the evolution of NO might be due to the too rapid reaction between the Cu and $HNO_3$, dilute solutions of the latter, 10 %, 5 %, and 2½ % concentrated $HNO_3$ solutions, (10cc conc. $HNO_3$, to 90cc $H_2O$, etc.) were used consecutively and pulverulent copper added. In each case nitric oxide was evolved, showing that the reduction, if any, was not complete. Tests were also made in each case for $NH_3$, but nothing more than traces was detected (coloration of litmus). That the reaction might be still slower, a clean copper strip was placed in the 10 % $HNO_3$, solution and left there for two days; no ammonia was produced, though there were no visible red fumes. These experiments were then varied by (1) the addition of $KNO_2$ for nitrites, (2) by the addition of $KNO_2$ and bubbling of $H_2$ through the solution and (3) by stirring. The results were negative. Again they were varied by the addition of $H_2SO_4$ to the solutions

containing the pulverulent Cu and the copper strip and stirring, still with no results.

Attention was then turned to the electrochemical side of the subject. Accordingly, a 5 % solution of $HNO_3$ was electrolyzed between copper electrodes at a current density of 8 amp/qdm.[2] Gas was evolved freely at the cathode, judging by the smell, it was nitric oxide. Also, $NH_3$ was formed in detectable amounts.

It was noticed in connection with this experiment that gas was evolved freely at the cathode and that the gas was probably NO; that no gas was evolved at the cathode when a platinum anode was used from the beginning; that even with a copper anode no gas was evolved at the cathode until the solution of $Cu(NO_3)_2$, collecting in the bottom of the vessel due to its greater specific gravity, reached the bottom of the cathode. Then, at that point, gas was evolved. This evolution of gas continued after the electrolysis was stopped. These phenomena were noticed repeatedly. To determine the composition of the gas given off at the cathode the following experiment was made.

In a gas coulometer were placed two copper strips as electrodes, connected in circuit by wires thrust through the stopper which closed the coulometer. The lower parts of the electrodes were coated with paraffine to prevent short-circuiting. The coulometer was then filled with 10 % $HNO_3$ solution and a current was passed that gave a density of about 8 amp/qdm. As soon as the concentration of the $Cu(NO_3)_2$ became considerable, gas began to be evolved. Portions were withdrawn from time to time for analysis and showed the following composition:

$$NO = 80\ \%;\ H_2 = 3.\ \%;\ \text{Nitrogen (by diff.)} = 17\ \%.$$

NO was determined by absorbing the gas in 10% $FeSO_4$ solution; $H_2$, by palladium absorption. The residue was taken as nitrogen. There may have been some other oxides of nitrogen.

It became evident from the foregoing experiments that $HNO_3$ could not be reduced quantitatively to $NH_3$ in the presence of Cu ions and that the reduction stops at the nitrite stage. This was further established by an experiment in which a solution of $HNO_3$, composed of 100cc concentrated $HNO_3$ to 200cc $H_2O$, was electrolyzed between double platinum anodes and a small (2 x 5 cm) copper cathode. A current (7 amps) was passed of such

cathode density that no copper was dissolved. Under these conditions no gas was evolved at the cathode and the reduction to $NH_3$ was large. When the current density, however, was allowed to drop off so that some copper was dissolved, NO was given off abundantly at the cathode and a greatly increased current density was necessary to effect complete reduction again.

Upon such evidence, then, it was decided that the presence of Cu ions in solution prevented the reduction of $HNO_3$ to $NH_3$ and caused the production of nitrites when copper was dissolved in $HNO_3$.

Accordingly efforts were made to find some anion which would form an insoluble compound with copper cations as fast as the latter were thrown into solution, yet which would not inhibit the solution. If the Cu ions were precipitated as fast as formed, there should be a reduction to ammonia. To effect the chemical precipitation of the Cu ions the following substances were used, all giving, however, salts soluble in $HNO_3$ solutions:

Boric acid, phosphoric acid, sodium phosphate, benzoic acid, and potassium sulphocyanate. (The latter reduces $HNO_3$ to $NH_3$.)

An attempt which was successful, was then made to precipitate the Cu ions electrolytically as fast as they were thrown into solution by the chemical reaction between the acid and copper. The apparatus and operation were as follows:—10 % $HNO_3$, platinum anode, enclosed in parchment to prevent the oxygen there liberated from diffusing through the solution and causing convection currents; a copper or platinum cathode enclosed in a porous porcelain cup, containing as cathode liquid a solution of NaOH. The electrodes were placed as near as possible to the bottom of the cell. A copper strip was suspended in the $HNO_3$ solution and protected from polarization by two paraffine shields (filter papers covered with paraffine). The strip being suspended in the upper part of the solution and the electrodes in the bottom of the cell, there was less tendency for the current to pass through and polarize the copper. Any such tendency, however, would have been obviated by the paraffine shields. The copper nitrate formed by the chemical action flowed to the bottom of the vessel under the influence of gravity. A current of 1.5 amp. was passed through the solution which car-

ried the copper ions into the cathode chamber where they were precipitated by the NaOH, forming a coating of $Cu(OH)_2$ on the inside of the cup. The $NH_4$ ions were also carried into the cup where they were tested for by warming a portion of the solution and smelling. Good qualitative tests were obtained. Thus the concentration of copper ions was kept down and the copper then dissolved with but a slight evolution of gas.

That no nitrates were produced at anode was proven by electrolyzing a 10% solution of $HNO_3$, free from nitrites, with copper anode and platinum cathode, the latter enclosed in a porcelain cup containing NaOH solution, as above. After a run of one half hour the solution was tested for nitrites with KI, the copper first being removed by NaOH; no nitrates were indicated. A current of 1.5 amp. was used. Anode surface 5 x 10 cm.

An experiment was performed to determine the amount of gas evolved on dissolving a known amount of copper in nitric acid where no attempt was made to reduce the nitrites produced or to precipitate the ions formed, and to compare this weight and volume with those of copper dissolved under the conditions as obtained in the first experiment above described where the Cu ions are precipitated electrolytically. Accordingly a copper strip No. 1 of known weight was dissolved, partially, in 10% $HNO_3$ and the evolved gas measured in a gas burette. A like strip No. 2 of known weight was placed in a portion of the same solution but under conditions mentioned above, and the evolved gas caught and measured in an inverted coulometer.

| Amt. Cu dissolved. | | Gas evolved. | Time. |
|---|---|---|---|
| 1 | 1.25 gms. | 100 cc + | 2 hrs. |
| 2 | 0.30 " | 2.0 cc — | 3 hrs. |

If No. 2 had evolved gas at the same rate at No. 1, the volume should have been 25 cc instead of 2.0 cc; or, it may be said, 23 cc of NO were reduced to $NH_3$ by the hydrogen evolved by 0.3 grams Cu dissolving. $0.3 : 1.2 :: X : 100 : X = 25$.

This, then, establishes the fact that copper on dissolving in $HNO_3$ in the absence of copper ions does reduce nitric acid to $NH_3$.

The question was then suggested:—what accelerates the rate of solution of the copper in No. 1 over that of No. 2? Is it the presence of $HNO_2$ or of Cu ions?

To answer this an additional experiment was made. A copper strip of known weight was suspended in 10 % solution of $HNO_3$ composed of 10 cc conc. $HNO_3$ and 90 cc 2 M $Cu(NO_3)_2$, to which about 2 grams of urea had been added to decompose any nitrites formed. No gas was evolved, unless stirred; though small bubbles collected on the strip. This was No. 3. A second strip, No. 4, was suspended in a solution of same strength as above, containing nitrites ($NaNO_2$). These two compared with No. 1 show the following:

| Copper | dissolved. | Gas evolved. | Time. |
|---|---|---|---|
| 1 | ? | 6.0 cc | 1 hr. |
| 2 | 0.0176 (gain) | None | 1 hr. |
| 3 | 0.4 gms. | 90.0 cc | 1 hr. |

These results would show that the acceleration is due to the presence of nitrites.

The results of this paper may be summed up:—

1. When copper dissolves in nitric acid the anode reaction is the formation of copper nitrate and not of nitrite.

2. When copper dissolves in nitric acid, the cathodic reaction is the reduction of the nitric acid. The chief reaction product is NO when there is copper as ion in the solution, and $NH_3$ when there is practically no copper as ion in solution.

3. When a solution of copper nitrate and nitric acid is electrolyzed, with a copper cathode, nitric oxide is formed at the cathode.

4. When a solution of nitric acid is electrolyzed, with a copper cathode, ammonia is formed at the cathode.

5. The apparent discrepancy between the chemical and electrochemical action of copper on nitric acid is due entirely to a difference in the conditions under which the two sets of reactions have been performed.

This work was suggested by Professor Bancroft and has been carried on under his supervision.

*Cornell University.*

## DISCUSSION.

Dr. C. J. Thatcher: There was an investigation made in Germany two or three years ago by Müller on the effects of copper in the reduction of nitrates to nitrites and he found that with a copper cathode he got almost ninety per cent. reduction to nitrite, a yield which he could not get unless he had copper in the solution, or rather a copper cathode. Is it not possible that in this case there are always two reduction processes? That nitrous *acid* always forms, but is split up again into nitric acid except when you do not have copper present, and besides you have another direct reaction in which you get a reduction to ammonia. It strikes me that that may be an explanation.

Dr. Bancroft: I think there is no question but what that is right. In the case where you have nitric oxide formed, the reduction goes through the nitrous acid stage. In the other case it presumably does not go through the nitrous acid stage. If you take nitrobenzene, which has the formula of a substituted nitrous acid but which is stable, you find that it is reduced by copper to aniline. The difference is due to the instability of nitrous acid. In the experiments referred to by Mr. Thatcher, the reduction was carried on in a neutral or slightly alkaline solution.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

# AN ALUMINUM AND MAGNESIUM CELL.

H. T. Barnes and G. H. Cole.

In a previous paper[1] before this Society, by Dr. H. M. Tory and one of the authors, some electrode effects were described, which resulted from the action of dissolved gases in water on metal surfaces. Thus two electrodes of the same metal when immersed in gas-free water showed zero potential relatively to each other, but when one of the electrodes was surrounded by gas-charged water a considerable difference of potential resulted. Where the gas dissolved in water was oxygen or air, the electrode in the gas-charged water was always the cathode. In the case of hydrogen, the electrode was sometimes anode and sometimes cathode, depending on the metal.

In general the results previously obtained showed that, of all the gases used, oxygen or air gave the most pronounced results; that electrodes of the same metal could always be brought to zero potential by expelling the dissolved gases, or by surrounding by gas-free water; that in oxygen the most easily oxidized metal, magnesium, gave the smallest result, while aluminum which does not oxidize easily gave the largest result; that an aluminum electrode artificially oxidized gave a difference of potential against a clean aluminum electrode of only one half that observed between two clean aluminum electrodes, and that the metals like platinum and palladium were the most difficult to bring to zero potential after being treated with gas-charged water. The effect appeared then to resemble more of an occlusion phenomenon than an actual oxydation of the metal surface.

After obtaining measurements of the difference of potential between gas-free and gas-charged water for electrodes of a large number of metals, several pairs of dissimilar metals were tried. The difference of potential was obtained on an elec-

[1] Trans. Am. Electrochem. Soc., *3*, 95 (1903).

trometer when the combination was immersed in gas-free water, and then in gas-charged water. From the previous effects obtained on the metals separately the combined effect could be calculated, and was found always to agree with the observed value. One of the combinations tried was of so much interest that it has formed the subject of a further study, and the main results obtained are described here.

The E. M. F. developed by the cell which we have produced depends on the fact that aluminum electrodes give the largest effect in oxygen-charged water of any of the metals observed, and magnesium gives the least. Hence, when a magnesium and an aluminum electrode are placed in oxygen-free water a small difference of potential is developed since they are close together in the potential series; but when the same electrodes are placed in water containing dissolved oxygen a large difference of potential results. As an example, we found that when the O-free water was charged by allowing O gas to bubble through, or by adding a few drops of hydrogen peroxide, the potential between Al and Mg rose from 0.2 to somewhat over 1 volt; in both cases the Al remained the cathode.

To compare separate results with this we found that the potential between Al electrodes in O-free and O-charged water was about 0.8 volt, while that between Mg electrodes was only 0.02 volt. Hence to the initial difference between Al and Mg electrodes of 0.2 volt, in O-free water, must be added the increased negative charge developed on the Al surface of 0.8 volt in the presence of dissolved oxygen. Magnesium was the only metal we tried above the aluminum in the potential series.

The other metals decompose water so readily that they are inconvenient to work with. Any of the metals we tried which were below aluminum in the potential series, and to which Al is anode, gave results depending on the relative positions of the metals.

A metal like lead placed with aluminum gives in O-free water about 0.8 volt. In O-charged water this is entirely removed and the two electrodes come to zero potential, since the Al is the anode and the presence of the dissolved O gives to it a negative charge about equal in amount. In a similar way when a zinc electrode is used with aluminum the initial potential difference

in O-free water, Al being the anode, is reduced to zero, and then changes sign. In order then that the presence of dissolved air or oxygen may increase the voltage of a cell, containing Al as one electrode, it is essential to select a metal for the other electrode higher in the potential series.

We decided to study a combination of the metals Al and Mg for the reasons just set forth, and consequently experiments were undertaken to see how far the cell might be improved.

One of the most interesting features of the cell is that on shortcircuiting the electrodes, the voltage and current steadily increase to maximum values, depending somewhat on the electrolyte used or the resistance of the cell. Thus Al and Mg in an electrolyte of alum, to which is added some hydrogen peroxide, gives an E. M. F. of from 1.2 to 1.4 volts. After the cell is short-circuited for some time, five or ten minutes, this increases to a value from 1.6 to somewhat over 2.0 volts. Continued short-circuiting apparently depletes the supply of dissolved O in the solution, and the E. M. F. falls slowly after passing through the maximum value. Further addition of O, such as adding more peroxide, causes a rapid increase to the higher value to be followed by a slow drop when a current is drawn. When the electrodes were separated by a porous partition the addition of peroxide to the electrolyte surrounding the magnesium had no effect on the E. M. F. The whole effect was thus centered on the aluminum.

Several electrolytes were tried to secure the maximum results, and it was hoped that one could be found which would reduce to a minimum, the slow wasting away of the magnesium metal. From a large number of trials the best results were obtained with a solution of aluminum sulphate surrounding both electrodes. A double fluid cell was prepared with magnesium sulphate around the magnesium, and aluminum sulphate around the aluminum, but the presence of the porous pot increased the resistance of the cell, and did not seem to add anything of value to the combination. It was found necessary always to withdraw the Mg electrode from the electrolyte when the cell was not in use. The aluminum salt crystallized around the Mg, and protected it from the action of the air, thus keeping it clean and bright for further use.

Cells were usually made from sheet aluminum bent around so as to give a large surface. The magnesium was used either in the form of ribbon coiled around a light wooden or ebonite frame, or in the form of rods about a centimeter in diameter. Cells were made also in containing vessels of aluminum about the size of an ordinary drinking glass, two or three rods of magnesium supported on a sliding stand serving for the anode. Such a cell when put together with a solution of aluminum sulphate of maximum conductively developed an E. M. F. at once of 1.58 volts. On adding peroxide of hydrogen the value rose at once to 1.77 volts, and after short-circuiting for a few minutes gave a value of 2.2 volts.

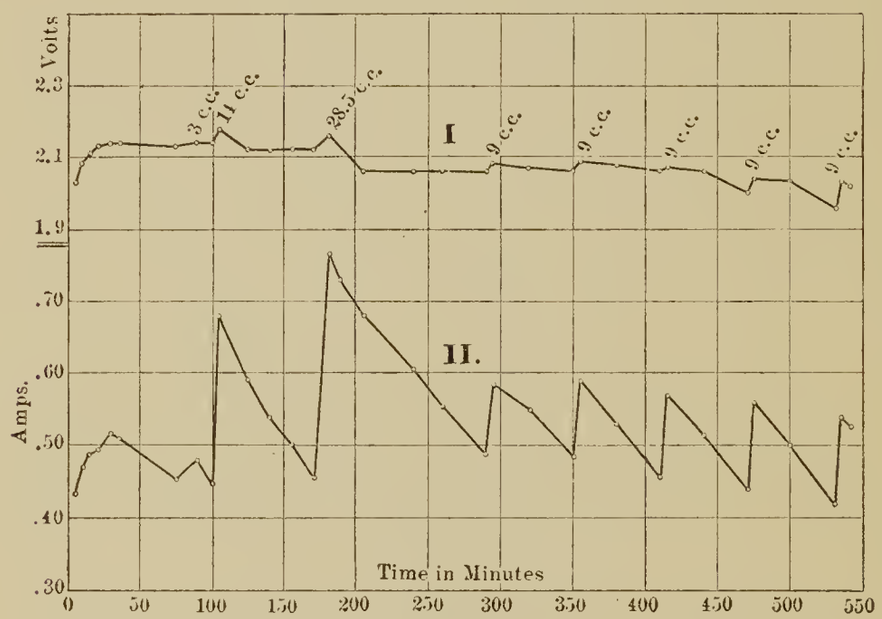


FIG. 1

The cell was tested for current capacity with 10 c. c. of peroxide added to 450 c. c. of electrolyte. The current was read on a 1 to 10 range ammeter (Weston millivoltmeter with shunts) to which the cell was attached direct. From 0.4 ampere the current steadily rose to 0.52 ampere in half an hour. On adding a few drops of sulphuric acid to the cell as much as 4 amperes was obtained, but the action became unpleasantly violent on the magnesium electrode.

A nine hour test was made on a cell in order to obtain the amount of magnesium consumed. Two identical cells were constructed, one to be used for the current test and the other to be left undisturbed to allow for the natural wasting away of the

magnesium. From the working cell the current was kept constant by adding, from time to time, fresh quantities of peroxide. The results of the test are shown in the accompanying figure, where the curve for volts is placed over that for amperes on the same time base. The addition of each quantity of peroxide is shown by the series of peaks. The average ampere efficiency was found to be about 64%. The loss in efficiency due to the natural wasting of the magnesium was about 13%.

The rise of E. M. F. exhibited by this cell seems to be connected with the removal from the surface of the aluminum of the exceedingly thin film of oxide, or hydroxide, that apparently always forms on a surface of aluminum. This film has already been the subject of numerous investigations. Drawing current from the cell or sending a current through the cell in the same direction from an outside source reduces the film and hence the resistance of the cell, but in addition it in some way augments the E. M. F. by removing a substance which is itself electro-positive to aluminum, and leaving a clean untarnished surface to the action of the oxygen in solution. If a current is sent through the cell in a reverse direction, so as to make the aluminum the anode, the film on the surface at once forms, and increases just as in the case of the well-known aluminum alternating current rectifier.

*McGill University.*

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## DISCUSSION.

Mr. Morris Loeb: I desire to ask Prof. Bancroft whether the magnesium and aluminum were chemically pure; when impure, both of them are, of course,, likely to react with water and form hydroxides. While it is possible to regard both of these as electro-positive, it must be remembered that there is a definite tendency toward the formation of a spinel between these two compounds, whose precipitation would compensate for the comparatively slight solubility of the hydroxides in the first place. It might, therefore, be possible enough that there are two superposed reactions, one of which was virtually the decomposition of water, resulting in a hydrogen and oxygen cell.

Dr. W. D. Bancroft: There is nothing said in the manuscript as to the purity of the aluminum. I assume that it was sheet aluminum as found in the laboratory. The greatest result is obtained when the electrode is oxidized.

Mr. Loeb: It seems to me that the high voltage cannot be explained satisfactorily by reason of the difference of potential of the two metals in contact with water. If we assume, however, that the reaction between the metals and the liquid is not of an electrolytic order, we then have the hydrogen and oxygen cell and the cell composed of the two hydroxides, in their spinel-making relation to account for the peculiar results. The time curve seems to me to indicate that there is a non-electrolytic reaction modifying the conditions.

The one thing I feel competent to point out is this: that although magnesium and aluminum are ordinarily taken as metals belonging to the same general class, this is only true under limiting conditions; as soon as reaction with water takes place, the two hydroxides have such different functions that it is possible to conceive of a hydrogen-oxygen or hydrogen-hydroxyl cell being formed, under conditions differing from the ordinary ones. If, now, the concentration of the two hydroxides is further affected by a mutual reaction forming spinel, we would have a second kind of potential involved and, consequently, the total resultant might readily give an intermittent curve. If the reaction were purely electrochemical, such variability of potentials could not be expected.

Prof. Bancroft: There is another case which might have a bearing on this. At the meeting in Philadelphia, Mr. Carhart called attention to a cell consisting of Ni/dil. $Ni/SO_4$ conc. Ni $SO_4/Ni$. If that were a concentration cell, and it is on paper, the current ought to flow through the solution from the dilute solution to the concentrated solution.

As a matter of fact when Mr. Carhart tested it he found that the current flowed in the opposite direction. The reason for that has been shown to be that this is not a concentration cell at all, but that it is an oxygen cell. If you keep oxygen out of the solution you can get results much more in harmony with the theory; and it has also been shown that oxygen corrodes nickel faster in the presence of a concentrated nickel sulphate solution than it does in the presence of a dilute nickel sulphate solution.

Those things could not be foreseen, but they actually occurred and it is not impossible that we are dealing with some similar case.

DR. THATCHER: I would like to ask whether the author stirred the solution when making these measurements?

DR. BANCROFT: I imagine not, except to the extent that in some cases he bubbled oxygen through.

DR. THATCHER: That would not make the cell completely homogeneous.

PROF. BANCROFT: As I understand it, the problem is not why there should be fluctuation in the voltage—that I think is easily explained; but why you have a voltage of 2.1 or thereabouts.

MR. SPERRY: Is there anything said as to how the oxygen is put in there?

PROF. BANCROFT: They either added hydrogen peroxide or bubbled oxygen through.

MR. SPERRY: It does not matter. It is agitated.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

# MELTING POINTS OF SOME CRYOLITE-ALUMINA MIXTURES.

By Francis R. Pyne.

During the spring of the present year, the writer together with Mr. Y. F. Hardcastle, conducted experiments on the melting points of various mixtures of cryolite and alumina.

Commercial cryolite was used in the experiments, no analysis being made. The alumina was obtained in the form of calcined bauxite, and by analysis contained 99.9 o|o pure $Al_2O_3$.

The heating apparatus consisted of a gas-fired furnace, ordinary illuminating gas furnishing the fuel. The charge was contained in a graphite crucible, made by boring out a solid graphite rod. The outside of the rod was then turned down to fit a No. 3 plumbago crucible. The space between the two crucibles was tightly packed with powdered graphite.

The cryolite and the alumina were finely powdered and thoroughly mixed in the proper proportions. A weight of one hundred grams was used for each determination.

Temperature readings were obtained by the use of a Le Chatelier Pyrometer, and were taken at intervals of fifteen seconds, that interval being found most satisfactory.

The determinations were made by placing the sample of one hundred grams in the double crucible, which was then placed in the furnace and the thermo couple inserted in the mixture through a hole in the furnace cover.

The mixture was then melted and when thoroughly fluid, the gas was turned off and the mixture allowed to cool, all openings in the furnace having been closed in order to prevent access of air, and decrease any oxidizing effect as far as possible. The temperature readings were then taken at fifteen second intervals, as previously stated, a stop watch being used for the sake of greater accuracy. The readings were taken until the mass had thoroughly solidified.

It was found to be impossible to obtain any satisfactory results with a rising temperature, due to the uneven heating of the crucible, the blast pressure varying considerably, and it was also found that the same charge could be used but twice at the most, due to oxidation on heating.

An objectionable delay was caused by the thermo-couple becoming very brittle after being in the molten mixture, and breaking unless the utmost care was used in inserting and removing it. This brittleness had, apparently, no effect upon the accuracy of the pyrometer, as frequent standardizations gave practically constant values. It was found that, upon heating the mixture to a temperature of 1,100° or higher, the cryolite decomposed.

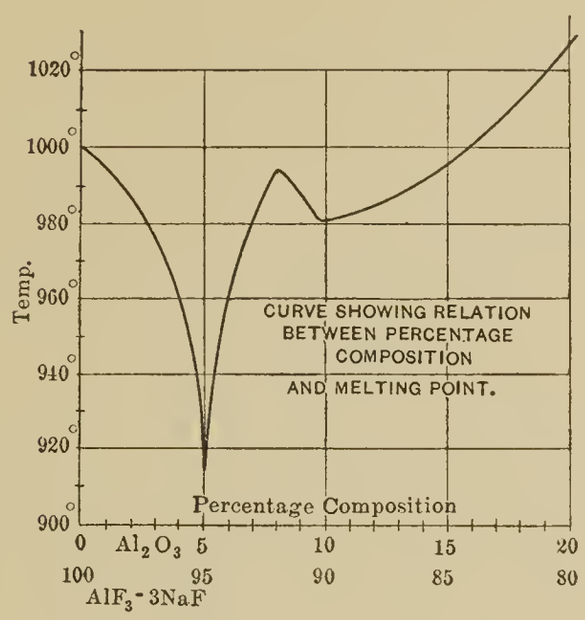
The cooling curves plotted from the data obtained, were found to be quite smooth, the decrease in temperature being practically constant until the material began to solidify, when the temperature remained stationary for five or six readings, and in some cases, for as long a period as three minutes, although a weight of but one hundred grams was taken.

The more important of the results obtained are given in the following table:

| Cryolite. | Alumina. | Melting Point. |
|---|---|---|
| 100 | 0 | 1000°C. |
| 97 | 3 | 974° |
| 96 | 4 | 960° |
| 95 | 5 | 915° |
| 94 | 6 | 960° |
| 93 | 7 | 982° |
| 92 | 8 | 992° |
| 90 | 10 | 980° |
| 85 | 15 | 994° |
| 80 | 20 | 1015° |

The curve plotted from the above data shows the most fusible mixture to be that of cryolite 95% with alumina 5%. At 96% cryolite there is a drop of but 40°, while the 95% mixture drops very suddenly, and as the percentage of alumina increases, rises very rapidly until 20% alumina makes the mixture more infusible than cryolite alone.

At 10% the temperature curve drops down to 980°, and then rises, showing the probable formation of a compound. As this drop is in the neighborhod of the cryolite 91% alumina 9%




mixture, the composition will be nearly $Al_2O_3$. .4 ($Al\ F_3$ .3 NaF). Owing to the limited time available, no mixture of the above percentage was made.

The writer's thanks are due to Prof. J. W. Richards, at whose suggestion the work was undertaken in the metallurgical laboratory of Lehigh University.

*Great Falls, Mont.*

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

# SOME SURFACE FACTORS AFFECTING DISTRIBUTION.*

By Harrison E. Patten.

## Introduction.

The relation between the absorptive power of a finely divided solid and the quantity of water retained by the individual particles within their own bodies, has been studied by van Bemmelen.[1] So far as we are aware, there is no set of data sufficiently complete to establish a relationship between the quantity of substance absorbed by the particles and the volume of solution which they retain in the spaces between the particles when the aggregate of grains is allowed to settle out of suspension and pack down. Consequently, a system has been studied to ascertain the effect of absorption upon the quantity of liquid a powder will retain in its capillary spaces.

*Experimental*—The solid was a quartz flour having the following mechanical analysis:

Table I.

Quartz flour: Mechanical analysis.

| Limiting diameters of grain (mm) | Per cent. by weight |
|---|---|
| 2-1 | 0 |
| 1-0.5 | 0 |
| 0.5-0.25 | 0.05 |
| 0.25-0.1 | 0.2 |
| 0.1-0.05 | 8.0 |
| 0.05-.005 | 86.2 |
| 0.005-.000 | 5.42 |

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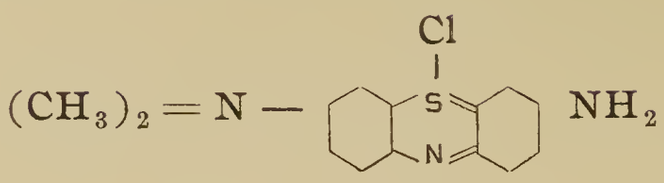
[1] Zeit. anorg. Chem., *23*, 112 (1900).

The dye used was gentian violet,




chosen because it has a high coloring power, because it suffers little or no change by contact with the quartz, and is absorbed by quartz to a very considerable extent.

The sample of gentian violet gave the characteristic reactions, viz.: (1) dilute aqueous acids, as hydrochloric or nitric acids, turn the aqueous dye from a violet to green; (2) concentrated sulphuric acid dissolves the dye, forming a yellowish-green solution; and (3) aqueous sodium hydrate gives a violet color.

Each system was made up of 100 grams quartz flour, 150 cubic centimeters water, and a definite weight of dye.

After several preliminary experiments, using a thermostat regulated to 0.1 of a degree, Centigrade, it was found that the factor of error produced by insufficient agitation ( in the thermostat) of the bottles containing the quartz and dye solution, and by the necessity of centrifuging these bottles at room temperature to insure settling after complete mingling of quartz and solution had finally been secured, rendered the thermostat useless for the present purpose. The experiments were accordingly carried out at room temperature, about 25° C.

In addition to determining the concentration of the solution remaining above the quartz flour, its volume was measured; that is, the volume of the liquid which could be drained off from the quartz after the bottle containing the system had been centrifuged at high speed for about ten hours and then allowed to stand some six weeks upon the shelf. This liquid, remaining above the quartz, could be poured off cleanly, and measured to within 0.3 cubic centimeter, since the quartz had settled into a compact mass in every bottle used. This volume subtracted from the 150 cubic centimeters originally added, gives the liquid retained in the pore spaces between the quartz particles. The dye was estimated colorimetrically.

TABLE II.

Quartz flour, gentian violet, and water: 100 grams quartz, 150 cc. water, temperature, 25° C.

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| Grams dye added. | Grams dye absorbed by 100 grams quartz. | Grams dye left in 100 cc. solution. | Volume of solution retained by 100 grams quartz. cc. |
| 0. | 0. | 0. | 36.5 |
| 0.006 | 0.006 | trace | —— |
| 0.015 | 0.014 | 0.0001 | —— |
| 0.019 | 0.017 | (0.0001+)* | 36.0 |
| 0.038 | 0.036 | (0.0002)* | 38.0 |
| 0.075 | 0.0743 | 0.0004 | 48.0 |
| 0.100 | 0.0984 | 0.00108 | 50.0 |
| 0.200 | 0.1901 | 0.0066 | 46.0 |
| 0.300 | 0.266 | 0.0224 | 40.0 |
| 0.400 | 0.289 | 0.0740 | 37.0 |
| 0.500 | 0.295 | 0.1370 | 34.0 |
| 0.700 | 0.297 | 0.2668 | 30.0 |
| 1.000 | 0.293 | 0.4710 | 29.0 |
| 2.50 | 0.290 | 1.475 | 29.0 |

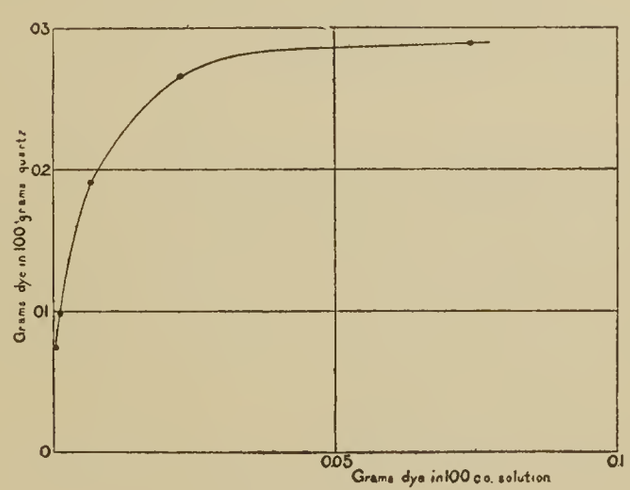



FIG. 1.

Table II gives the data. Column 1 contains the grams of dye added; column 2 the dye absorbed by 100 grams of quartz; column 3, the dye remaining in solution; and column 4, the volume of solution retained by the quartz. Figure I shows the grams of

*Interpolated.

dye absorbed by 100 grams of quartz, plotted against the grams of dye in 100 cubic centimeters of solution. The curve is apparently exponential in form, but does not correspond to a simple equation.

Figure II shows the volume of solution in the spaces between the quartz particles, as a function of the grams of dye held on those particles. During the first stages of absorption, this volume of liquid retained by the quartz changes from 36 cubic centimeters to 50, an increase of some 39 per cent. The maximum volume of liquid, 50 cubic centimeters, is held in the capillary spaces when about one-fourth of the gentian violet which the quartz can absorb has been taken up; and as more and more dye is absorbed on the grains of quartz, the volume of liquid between

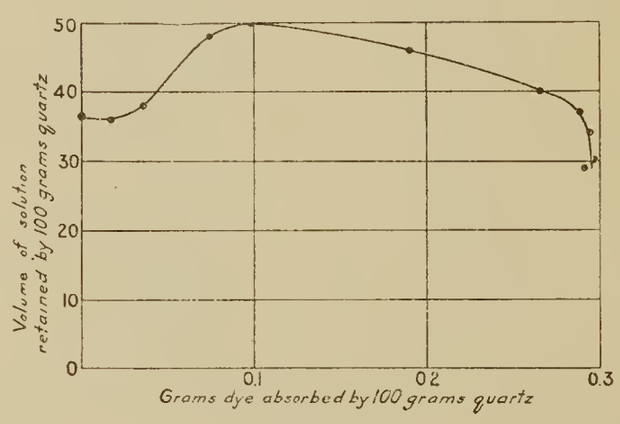



FIG. 2.

them gradually decreases, 'till only 29 cubic centimeters are held—7.5 cubic centimeters less than the volume of distilled water which 100 grams of this quartz flour retains.

In connection with this quantitative data, there is to be considered the state of aggregation of the quartz flour as it settles from suspension in the liquid.

At the maximum point of the curve in figure 2, the quartz flour settles more readily than in the bottles which correspond to the points each side of this maximum. And at high concentrations of dye in solution, the bottles must be centrifuged to clear the solution.

We are in no position to state the fundamental reasons for

either absorption or flocculation,[1] but a tentative hypothesis as to the interrelation of these observations is suggested.

1—It is a fact that when viewed under a microscope, the quartz flour is seen to abstract the dye, gentian violet, from dilute solution, and the particles then form into clusters. If the quartz be suspended in distilled water, and the dilute dye solution added from one side, the particles immediately at hand absorb the dye from solution and form into larger aggregates; and those particles at the other side of the microscopic field get no dye and remain as before, evenly distributed or deflocculated. The addition of dye to a body of quartz in quantity insufficient to satisfy its absorption capacity, leads to the formation of aggregates, and leaves a considerable part of the quartz in its original condition as individual grains. The more dye added, the more aggregates could be formed, up to a certain limit.

2—It is evident that as the number of the aggregates increases, the quartz as a whole will settle faster and faster; and when packed down by centrifuging, will occupy more and more volume, and thus leave room for more and more liquid in its capillary spaces; and this is what actually happens, as shown in Fig. II, the volume retained increasing to a maximum, 50 cubic centimeters.

3—The total surface of quartz grains exposed to the dye solution is decreased as the number of aggregates increases, so the absorptive capacity would be proportionately decreased in so far as it is due to surface effect.

4—We might expect, then, that the maximum absorption capacity of a powder clustered into aggregates would change if for any reason the clusters were broken up or separated into individual grains, with all their faces exposed to the solution. If this happened, it would be likely, too, that the particles of quartz would settle closer together, occupy less volume, and retain less liquid in their capillary spaces. Now Fig. II shows that this decrease in volume of solution held by quartz does take place, and with considerable regularity, as the quantity of dye absorbed by quartz increases.

[1] Whitney and Hosmer, Bull. No. 9, Division of Soils, U. S. Dept. of Agriculture (1897).
Briggs, Bull. No. 15, Division of Soils, U. S. Dept. of Agriculture (1899); also Jour. Phys. Chem., *9*, 617 (1905).
Cameron and Bell, Bull. No. 30, Bureau of Soils, U. S. Dept. of Agriculture (1905).
Schreiner and Failyer, Bull. No. 32, Bureau of Soils, U. S. Dept. of Agriculture (1906).
Patten, Trans. Am. Electrochem. Soc., *9*, (1906).
Buckingham, *ibid*, *9*, (1906).

Several experiments were tried with quartz flour and sodium eosine in aqueous solution to ascertain the form of the distribution curve for sodium eosine between quartz and water, and the volume of liquid which quartz holds under these conditions.

The results are given in Table III, and show that the quantity of sodium eosine absorbed by quartz flour is a linear function of the solution concentration. The volume of solution retained by the quartz, too, is in every case less than that of distilled water, as shown in Table II; and every concentration of sodium eosine tried, deflocculates the quartz, which has to be removed from suspension by continued centrifuging.

At lower concentrations, the sodium eosine is much more easily washed out from the quartz than the gentian violet, as might be expected from their respective distribution curves.

To ascertain how much water this particular sample of quartz flour would absorb from an atmosphere saturated with water vapor at the temperature of the laboratory, a fifty-gram portion of the quartz was placed in a shallow dish and kept in a covered glass vessel over water, and the gain in weight determined. The quartz absorbed 0.8 per cent., by weight, at 28°, corresponding to a partial pressure of water vapor of 28.1 mm.

TABLE III.

Quartz flour and sodium eosine, 100 grams quartz and 150 cc. solution.

| Grams dye added. | Grams dye absorbed per 100 grams quartz | Grams dye per 100 cc. solution. | Volume of solution retained by 100 grams quartz. (cc) |
|---|---|---|---|
| 0.00496 | 0.0009 | 0.0027 | —— |
| 0.0150 | 0.00135 | 0.0091 | 30.0 |
| 0.0496 | 0.0084 | 0.0274 | —— |
| 0.150 | 0.0348 | 0.0768 | 29.0 |
| 1.50 | 0.420 | 0.720 | 29.0 |

If we assume that 100 grams of quartz flour holds absorbed upon its surface, 0.8 gram water, or 0.8 cubic centimeters, when saturated with liquid water, as well as when in equilibrium with saturated water vapor, then it is clear that the larger volume of liquid held by the quartz when settled from suspension is contained mostly in the interstitial spaces as capillary liquid.

Parks has shown[1] that glass wool saturated with water vapor evolves no heat when placed in liquid water, although the same glass wool when dry gives 0.0011 calorie per square centimeter of its surface. In another paper[2] he states that the *apparent* specific heat of water in contact with a solid is approximately $(1 - \frac{A}{W} \cdot \frac{h}{T})$, where A is the area of the surface of the water in contact with the solid, w is the mass of water, h is the heat evolved per square centimeter at the surface of the solid and liquid (Pouillet effect), and T is the absolute temperature. From this, it is evident that if the mass of water is small, compared to the mass of powder, the variation in the apparent specific heat may be very great, so that it is not necessary to assume, as Martini[1] did, that some of the water is solidified on the surface of the powder, in order to account for the apparent variation in the specific heat.

Both of the above considerations support this assumption, which, of course, is not rigid, since it is necessarily modified by the fact that the grains of quartz touch each other and hold water in the solid angles thus formed, and obviate the possibility of a surface layer of liquid of uniform thickness over all the grains. Still, this experiment on the absorption of water vapor from a saturated atmosphere gives a rough idea of the quantity of hygroscopic liquid which the quartz holds when saturated with dye solution. And when taken with the other considerations, already advanced, it shows that the increase in volume of the settled quartz flour, as the quantity of dye absorbed is increased, is due to a change in the state of aggregation of the quartz particles, rather than to a union of the dyed quartz particles with water to form hydrated particles occupying a larger volume than the individual quartz grains.

This property of a settled-out solid, viz., of varying its apparent volume as the strength of the supernatant liquid varies, is not confined to quartz in dye solution. It is a very general phenomenon, exhibited by acids, bases, and neutral salts with finely divided solids and soils.

Some of the factors which must be considered in future work along this line are:

[1] Phil. Mag., (6) *5*, 519 (1903).
[2] Phil. Mag., (6) *4*, 240 (1902).
[1] Atti del R. Instituto Veneto, *8* (1896); *9* (1897); *12* (1900).

1—Accurate chemical data upon the quantity of solute or radicle absorbed from solution by the suspended powder.

2—Final concentration of suspending solution.

3—Acid or basic nature of the powder and of the solute used.

4—Measurement of the volume of solution retained by the powder when settled from solution under fixed conditions.

5—Measurement of the time rate of settling for the same weight of powder in the different concentrations of solution used.

6—Measurement of the volume of liquid retained by the settled powder in different *pure* solvents, as compared with the rate of settling of the powder in these solvents.

7—Accurate control of temperature.

8—Measurement of the electrical conductivity and other physical constants of the final concentration of solution reached after the powder had exercised its absorbing power.

9—Quantity of liquid which the dry powder will absorb from a saturated atmosphere of the liquid.

10—Lowering or raising of surface tension of liquid, produced by dissolving the given solute in it.

11—Possible hydrolysis of the solvent or solute; or decomposition under the influence of the greatly extended surface offered by the powder.

Thus it is clear that the form of curve representing the distribution of solute between powder and solution will be very considerably modified by the change in surface which the powder undergoes as it flocculates or deflocculates with the changing concentration of the solution.

*Bureau of Soils,*
*U. S. Dep't of Agriculture, Washington, D. C.*

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 9, 1906, President Hering in the chair.*

# PYROMETERS.

By E. F. Roeber.

In view of the increasing importance of pyrometry in the chemical and metallurgical arts, it has been thought interesting to have at this meeting an exhibition of some of the more important modern commercial types of pyrometers. While this exhibition is not at all complete, it is fairly representative. We also have the pleasure to have with us, to-day, some specialists in pyrometry who will address you later. Under these circumstances, I will endeavor to be as short as possible in the few introductory remarks which I wish to make on the definition and measurement of temperature.

First, concerning the definition of temperature. Our senses tell us whether a substance or a body is hot or cold, but they do not give us a temperature scale. All measurements of the temperature of a body are essentially based on using a body of comparison, which is called a thermometer or pyrometer. We bring this in contact with the body, the temperature of which is to be measured, and we wait until thermal equilibrium is established. As thermometric substance, we use a body that has some property which changes greatly when the body is heated or cooled. This variable property we employ for the temperature scale. Thus, in a gas thermometer, the absolute temperature is directly given by the volume of the gas at constant pressure.

It is important that thermal equilibrium is established between the substance under test and the thermometer before a reading is taken. This point is especially to be considered with recording instruments when used in cases of rapid temperature changes. A sensitive thermo-electric pyrometer, for instance, will follow, immediately, all changes of temperature in air during a thunderstorm. It may show a sudden drop of temperature, for instance, while a mercury thermometer will show, at the same time, a less

sudden drop, simply because it is not able to get immediately into thermal equlibrium with the surrounding air.

The use of a thermometer makes us dependent on the substance of which the thermometer consists, mercury, gas, platinum, etc. We may choose two fixed temperature points. Then, different types of thermometers, when properly calibrated, will give, correctly, the temperature at these two fixed points, but there will be variations at other points, though they may be small. Now, there would really be no reason why one substance should be better as a thermometric standard than another substance, if we had not the fact that the laws which govern the so-called perfect gases are so simple and uniform that we conclude that these regularities are based on a simple and uniform constitution of gases, and the temperature uniformly indicated by them we define as *the* temperature. This is the only reason why the gas-thermometer temperature is made the standard.

But, after all, it is an arbitrary standard. Even those gases which are almost "perfect," show slight differences, and if we want to take those into consideration, then we are "up in the air" with our definition of temperature, and we cannot get on solid ground, except we get free altogether from any arbitrary thermometric substance. We need a temperature scale which is absolutely independent of any special substance.

This can be accomplished in no other way but by using the second principle of thermodynamics, in its most general form, where it does not depend on any special substance. This leads to the so-called thermodynamic temperature scale of Lord Kelvin.

When stripped of all mathematical refinements, the situation is simply this: We have the second principle of thermodynamics, and we elevate it to the rank of an absolutely true dogma. In any equation by which the principle may be expressed, or in any formula which may be derived from it, the absolute temperature, T, of the thermodynamic temperature scale is an independent variable—not the temperature, $t$, of any arbitrary temperature scale. On the other hand, what we observe and measure is the behavior of a substance, or function of the temperature, $t$, on the scale of that arbitrary instrument which we may use (mercury thermometer or electric resistance pyrometer, etc.).

Now assume we have an equation which is a strict consequence

of the second principle of thermodynamics and assume that every quantity in this equation can be exactly measured, at least if $t$ is substituted for T. Then, if we find that the equation does not come out exact numerically, we conclude that the disagreement is due to the fact that $t$ and T are not identical, and that our substitution of $t$ for T was wrong.

But this conclusion places us at once in a position to determine $t$ as function of T, for, in the original equation (which contains T as an independent variable), we may set $T = f(t)$, so as to get $t$ (instead of T) as independent variable. Then the new equation will be a differential equation which enables us to determine $f(t)$ as function of $t$, since all differential quotients, with respect to $t$, which appear in this equation, are directly measurable quantities.

In this way, we can determine, experimentally, T as function of $t$, or, in other words, we are enabled to reduce experimentally any arbitrary temperature scale ($t$) to the absolute thermodynamic temperature scale (T). The latter is independent of any arbitrary substance, and depends only on our fundamental supposition that the second principle of thermodynamics, in its most general form, is exactly correct.

How this method of reducing $t$ to T, works out mathematically for different equations which are consequences of the second principle of thermodynamics, has been shown in detail and with great clearness by Prof. Planck in his book of thermodynamics.* But not until these theoretical possibilities of reducing $t$ to T are experimentally realized, can we claim to have established an exact absolute temperature scale.

While thus the situation, with respect to a scientific definition of temperature, still leaves very much to be desired, enormous progress has been made in recent years, in engineering practice, in the invention and application of thermometers and pyrometers. We have now, decidedly, a pyrometer boom, and, different from certain other booms, this one is bound to last and grow, since pyrometry is an essential inherent part of that omnipotent tendency which makes exact principles, measurements and calculations the fundamental basis of all modern engineering work. And best of all, those very great difficulties, sketched

* Max Planck, Vorlesungen über Thermodynamik (1897), § 160 to 164 and 177.

above, which confront us in the problem of an exact scientific definition of temperature, are wholly insignificant in the practice of pyrometry.

For all practical purposes, the gas-thermometer scale is perfect, and by comparison with its scale, we can calibrate any other pyrometer. We need some fixed points, and we have them very conveniently in the fusing points of pure metals or of well-defined alloys, as well as the boiling points of certain compounds.* But it is evident that there should be an international agreement concerning the figures for these fixed points. An instance has come to the attention of the author where the figures, used for a certain point by the Bureau of Standards, in Washington, and by the German Reichsanstalt, agreed with each other, while a different value was used in France for pyrometer calibration. This must necessarily lead some day to confusion. That uniform values should be used, is far more important than that the values should agree with absolute exactness with the temperature scale.

The pyrometers which are here on exhibition, represent a number of quite different types. Without going into any description, I will mention the underlying principles.

The action of the ordinary mercury thermometer depends on the fact that the expansion of mercury, under the influence of heat, is greater, by a great many times, than the expansion of the containing glass tube and scale. This principle of the difference of expansion of two different materials, is made use of in a novel way in two pyrometers exhibited by Messrs. Edward Brown & Son. One is a recording pyrometer, a modification of the Brown hot-blast pyrometer. The other is the Brown quick-acting platinum pyrometer.

Of electric resistance pyrometers, two are here exhibited, both made by the Cambridge Scientific Instrument Co. One is provided with the Whipple temperature indicator, the other with the Callendar recorder.

Of thermo-electric instruments, we have here quite a collection. A Heraeus-Le Chatelier platinum-rhodium pyrometer is exhibited by Mr. Chas. Engelhardt. Then there are here quite

* Concerning some of the latest and best determinations, see, for instance, A. L. Day and E. T. Allen, *Physical Review*, Sept., 1904, and Palmer, *Physical Review*, Aug., 1905.

a number of types of the new pyrometer of Prof. William H. Bristol. The Price pyrometer, exhibited by the Electric Dental Specialty Co., is also a thermo-electric instrument.

Finally, we have here the Féry radiation pyrometer, exhibited by the Wilson-Maeulen Co. In contradistinction to optical pyrometers, in which the measurement is restricted to a single wave length within the visible spectrum (Wien's and Planck's laws), the Féry radiation pyrometer is based on the measurement of the total radiation (Stefan-Boltzmann law). I may mention that the Féry pyrometer is the first radiation or optical pyrometer which has been made recording. This success is due to the Cambridge Scientific Instrument Co.

Now, concerning the use of pyrometers in practice. We know that in many industrial, chemical and metallurgical processes, the maintenance of the correct temperature is absolutely essential.

Formerly, the manufacturer depended on the trained eye of the workman. The disadvantages are evident. One is that all the knowledge is stored in the workingman. When he leaves, the knowledge how to regulate the temperature leaves with him. On the other hand, if we use a pyrometer, we need to establish, once for all, the correct series of temperatures required for economical working, and make a record, and we can then duplicate this record all the time. The pyrometer makes us then independent of the personal equation of the furnaceman.

Further, recording pyrometers give us a method of control of the workman. We see, from the record, how efficient the different men are.

Moreover, if properly put up to the workingman, he will look at a pyrometer, not as a spy, but as a help. It gives him some guide to rely upon. Mr. Whipple, of the Cambridge Scientific Instrument Co., has proposed to establish a bonus system. A certain bonus should be paid to the workingman who keeps all the time within certain pre-determined limits of temperature.

In the old chemical and metallurgical arts, manufacturers were mostly satisfied to determine volumes and weights. The fact that so much more attention is now being paid to the measurement of temperatures in chemical and metallurgical engineering practice, indicates that these arts are now becoming what they ought to be—*applied physical chemistry.*

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 9, 1906, President Hering in the chair.*

# A THERMO-ELECTRIC PYROMETER FOR GENERAL INDUSTRIAL APPLICATIONS.

By F. F. Schuetz.

The William H. Bristol thermo-electric pryometer is the outcome of a demand for a comparatively inexpensive and practical pyrometer capable of withstanding rough treatment, and while perhaps not so accurate or capable of close reading as some types, is yet of sufficient accuracy to permit of extended application in the arts and answers a great many practical requirements. In fact, since the introduction of this type of pyrometer the field of pyrometry has been considerably enlarged, many unique applications being made.

Before describing the pyrometer and its applications, it might be well to indicate some of the requisites of a pyrometer suitable for industrial application.

(1) It is most necessary that the indicating device should be direct reading with visible scale and of such construction as to be capable of withstanding handling by people of ordinary intelligence.

(2) It must be comparatively inexpensive both as to first cost and cost of maintenance and so constructed as to permit of the ready replacement of any destructible parts, and this at small cost.

(3) It must be flexible or capable of being readily arranged for application to different places and for different purposes.

(4) It must eliminate the personal equation.

The William H. Bristol pyrometer has already been described at length before the American Society of Mechanical Engineers, and I will, therefore, dwell more in particular upon some of the details of construction as they bear upon the making of a pyrometer suitable for general industrial application.

The thermo-electric couple consists of two inexpensive metals

or alloys in the form of wires usually of 1-16 inch or ⅛ inch diameter, said couple giving an e. m. f. of about five times that of the standard platinum-rhodium couple.

The wire forming the elements of the couple is of sufficient diameter to avoid the introduction of any considerable resistance, and also to make negligible the resistance-temperature-error of the couple.

The couples themselves are protected in a rather novel and effective manner by first winding each wire with asbestos cord and then painting it with an insulating paint consisting of a mixture of powdered carborundum and a syrupy solution of silicate of soda. This insulation has proved perfectly satisfactory for temperatures up to 2000° Fahr., and is very simple and effective. The two elements are twisted and welded together at the hot end of the couple and left bare, so that there is practically no lag error. For higher temperatures and under conditions in which the insulation or couple is subject to injury, the couple thus insulated is inserted into suitable tubes of nickel, wrought iron, plumbago, porcelain, or the like.

Owing to the comparative inexpensiveness of the elements and of the method of insulating, these couples may be made of almost any desired length and used in any desired number—often in connection with but a single indicating instrument. Couples of a length of twenty feet are being used, and it will be readily understood that the first cost of a platinum rhodium couple of this length and with porcelain insulation, or a dozen or more shorter couples of this character, would be prohibitive. Where many couples are used upon one and the same indicating instrument, a suitable switching device is provided, so that the temperature at numerous points may be quickly determined by simply throwing the proper switch.

One of the most important features, however, in connection with these couples is the fact that it is not necessary to renew an entire couple in case of burn-out or other injury to the couple, but that only the active part called the "fire-end" or part exposed (usually only a small part of the whole length) needs to be replaced and this may be readily and quickly done and at but a fraction of the cost of the entire couple. It is but a small item to keep a stock of "fire-ends" on hand.

These fire-ends serve also as a means to check an active couple, it being only necessary to remove the "fire-end" which is in use and insert for a few moments one of the new ones.

This highly desirable feature of replacement is accomplished by making the couple separable in dividing it into two parts intermediate of the hot and cold end,—the "fire-end" or part directly exposed, and the "extension piece" or part not directly exposed to the heat and adapted to be fixed in a permanent position. The two parts are made of a length as required by the particular application and are connected by means

FIG. 1.

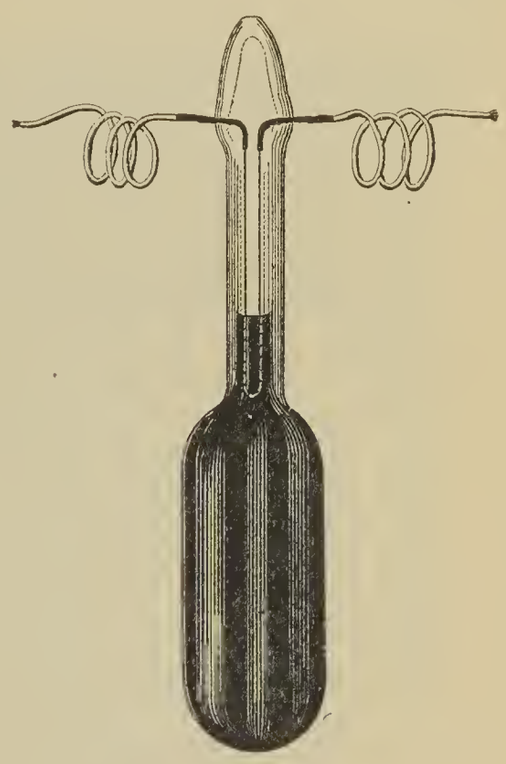


FIG. 2.

of the terminal pieces which are so arranged that it is impossible to incorrectly connect the two parts, see Fig. 1.

For certain purposes the elements of the couple are not joined or welded together at the hot end, but are separated and left exposed for a short distance, A small plate of copper, nickel or platinum is sometimes welded or soldered to the pointed separated ends, and this plate then touched to an object whose temperature it quickly assumes. For instantaneous response the hot end of the couple is reduced to the smallest possible size.

The terminals of the couple or its so-called "cold end" are connected by means of duplex flexible copper leads of

any desired length and of ample cross-section to a special low resistance milli-voltmeter made by the Weston Electrical Inst. Co., which is either of the wall type for indicating or recording, or of the portable type. The large station type is also used occasionally when finer readings are required. These instruments are direct reading with visible scale, of the pivot type with jewel bearings, dead beat, requiring no leveling or adjustment, and are capable of withstanding rough treatment.

The instrument together with leads and couple is of low resistance, the total resistance being in no case more than 10 ohms—nor less than 2 ohms. This fact allows the flow of a sufficiently heavy current to operate a pivot type of indicating

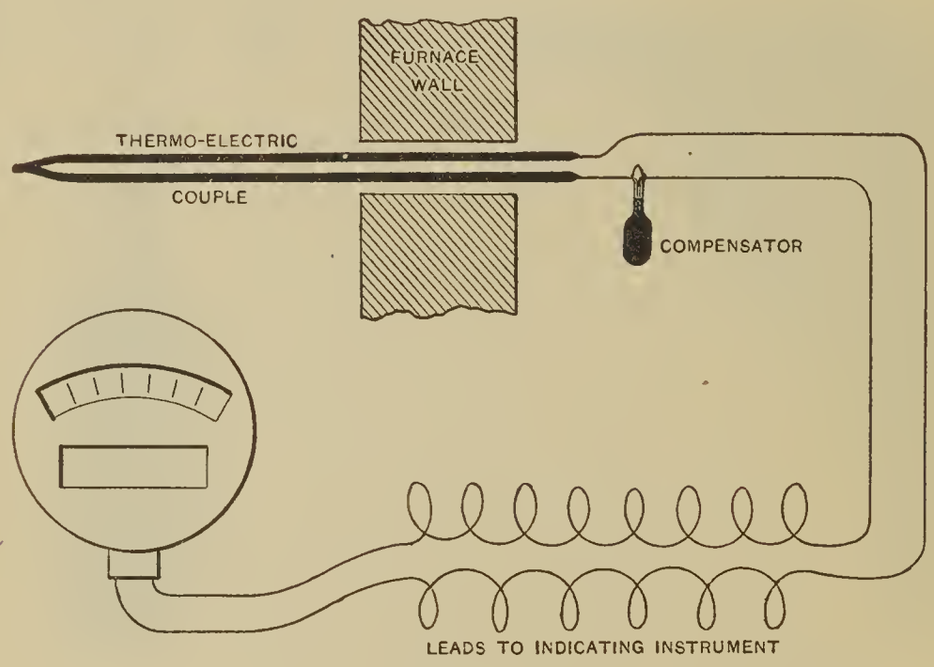



FIG. 3.

instrument such as the type described, and thus does away with the delicate suspension galvanometer which cannot be classed as an instrument suitable for industrial application.

Another important result of the low resistance feature is the possibility of being able to provide one and the same indicating instrument with several different scales by introducing different resistances in the instrument and providing the required binding posts.

The low resistance also makes practicable the automatic correction for the effect due to temperature variations upon the cold end of the couple. This is accomplished by inserting in series

in the circuit and in close proximity to the cold end of the couple, a mercury thermo-metric device, Figs. 2 and 3, which cuts in or out resistance in accordance with temperature variations, and thereby balances the change in thermo-electric effect and maintains constant the current flowing. This compensation is perfect only for a predetermined temperature, however, but is sufficiently accurate over a "working range."

Before discussing the industrial applications of the pyrometer, I should like to describe somewhat in detail Prof. Bristol's new

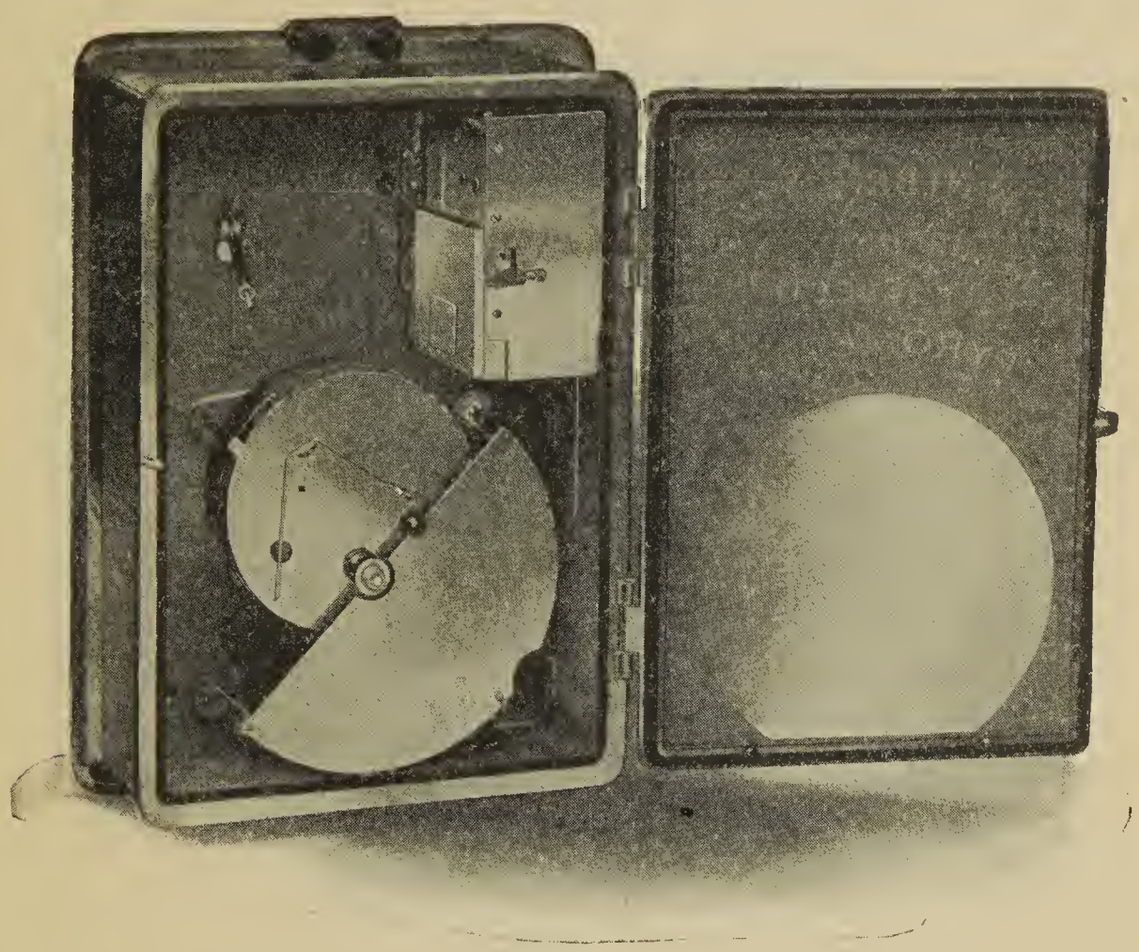


FIG. 4.

recording pyrometer, Figs. 4 and 5, which is also an extremely simple instrument and capable of withstanding ordinary wear and tear.

It is well known that the actuating current for the indicating arm derived from a thermo-electric couple is so small as to shut out all direct inking or any continuous direct contact of recording arm with chart. Prof. Bristol employs a specially prepared chart which is rotated by a suitable clock movement, and an electrical measuring instrument similar to the one previously

described, controlling a light recording arm provided with a marking point. The record chart is supported only over a portion therof, the remaining portion over which the recording arm acts being unsupported and perfectly free to vibrate. Vibration is periodically communicated to the unsupported portion of the chart by a tapping apparatus controlled by the clock movement. The marking point is normally free of this chart and comes in contact with it only during the period of vibration. Because of the delicacy of the recording arm, no attempt is made

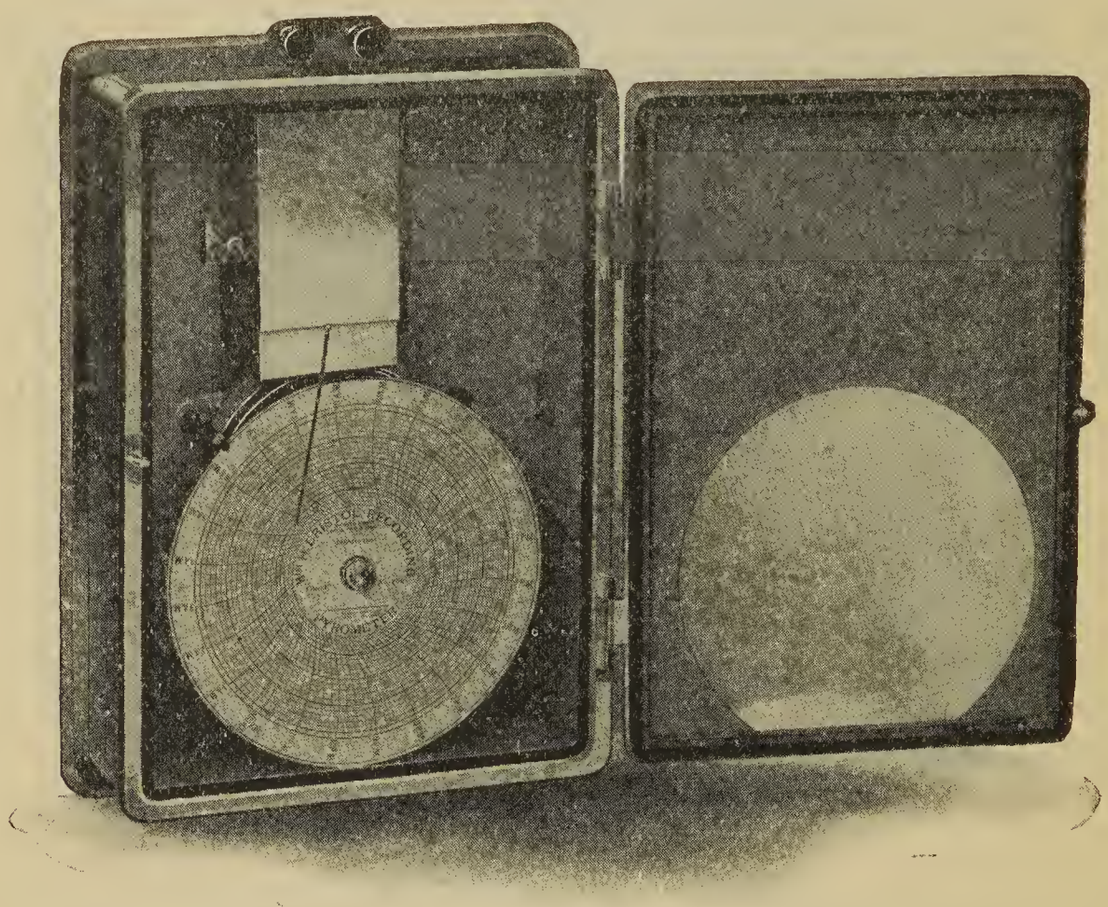


Fig. 5.

to ink with it, but through the vibration of the chart vibration is communicated to it so that the impact is gradually taken up by the recording elements and the pointed end of this recording arm caused to touch the chart. The chart itself is of the circular disk type, 8-inch diameter, such as used in the usual recording voltmeters, ammeters, pressure gages, etc., and is semi-transparently smoked over its active surface so as to only partly obscure the graduations. The surface of the chart is so sensitive

that it may be marked by a hair, and as the pointed end of the recording arm touches it a small amount of the soot is removed leaving a small white dot visible. The frequency of vibration is such that a continuous line is marked upon the chart by the recording arm. There is, therfore, but little strain placed on the arm and practically no friction between arm and chart to affect the sensitiveness of the movement of said arm, the contact being only momentary. After the record is complete the chart is removed and fixed by dipping into a fixative solution. This permanently fixes the record in a few seconds so that the charts may be filed away. The charts are readily removed and replaced by swinging outwardly the entire electrical instrument with attached recording arm as shown in Fig. 5. The said

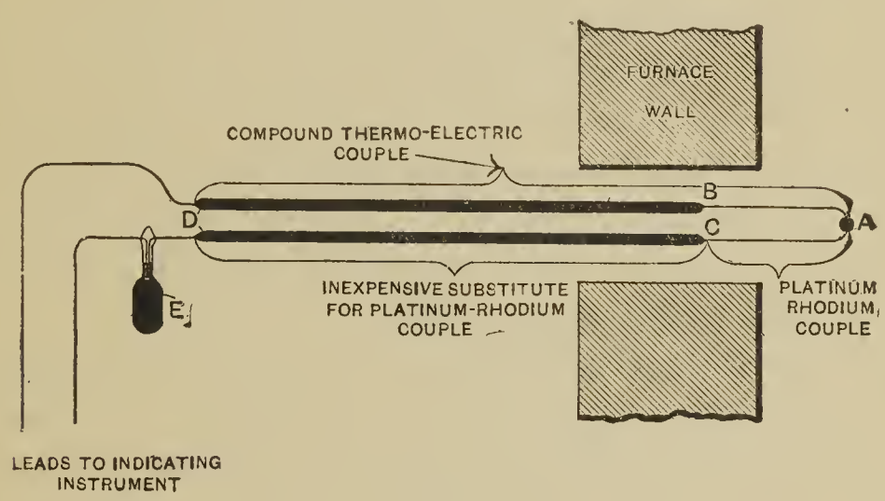



FIG. 6.

electrical instrument is entirely encased to protect it from dust, etc., the recording arm being brought through a small hole in the casing in the center line of the bearings of the actuating shaft. The clock movement and electrical instrument are further encased in a finished metal box with glass door through which the chart is visible.

For recording temperatures above 2000° Fahr. platinum-rhodium couples or platinum rhodium tipped couples must be used, as the cheaper metals and alloys cannot withstand continuous exposure to such high temperature.

The platinum-rhodium tipped couple, Fig. 6, is comparatively inexpensive as these expensive elements are made of just sufficient length to carry them beyond the most intense heat where

they are joined to the cheaper elements. By selecting the proper elements; or by properly arranging the cross-section or the distance of connections from the hot end of the couple, the secondary electro-motive forces set up at the connections of platinum-rhodium elements with the cheaper elements may be made to neutralize each other, and thus the affect of temperature at these points can be neglected. This feature considerably reduces the cost of the couple.

In connection with the recording instrument described, it might be added that this instrument may also be applied to the Féry pyrometer for the recording of temperatures above 3000° Fahr.

The difficulties in connection with the use of a pyrometer have been practical and are not inherent in the pyrometer as an instrument. A delicate galvanometer and a fragile, expensive couple can hardly be considered suitable for general industrial application. In fact, until recently the thermo-electric pyrometer was practically confined to the laboratories, and when industrially applied was only in the largest and most important works.

The following abstract of a letter received from the secretary of a certain glass works is instructive.

"We have used your pyrometers ever since we obtained them from you, and find that they give satisfactory results, being extremely sensitive, particularly for the heat we require, 800°-900° Fahr. We use a couple in each of our annealing ovens, both being connected with a switch, so that we can test the heat of our annealing ovens at once. We find that our men take great interest in these pyrometers, watching them carefully, and in consequence we get better results from our ovens in not having any of the goods fly or crack."

It is interesting to note that in one instance at least the workmen themselves have taken a positive interest in the pyrometer. The products of the ovens also have been improved, and there is an exactitude and confidence in the work which was impossible before the introduction of the pyrometer.

This experience has been repeated by many who have introduced a practical pyrometer into their operations.

It is very certain that many manufacturers were anxious to use pyrometers, but because of first cost, cost of maintenance

and repairs, great care and skill in handling, past experiences with pyrometers, etc., were extremely cautious. There was no necessity of educating those who have to do with the manufacture of iron and steel, tempering, hardening, annealing, blueing, or those engaged in the manufacture of brick, pottery, glass, etc., as to the value of an accurate knowledge of the temperatures with which they were working. They appreciated this full well, but the pyrometer could hardly have been said to have been an industrial article. With the introduction of cheaper and more practical forms of pyrometers, these people have seized the opportunity and have begun to install pyrometers throughout their works and consider them indispensable. Not only this, others have recognized the value of a pyrometer for their particular work, or have been educated to the point where they see the necessity for such instruments, and pyrometers may now be found in such establishments, as bakeries, jewelry factories, in the determination of the temperatures in the carburetters of gas plants, in tests of locomotives and steam boilers, the production of brazing powder, in connection with the rolling of sheet zinc, comparative tests of electric soldering irons, etc. In connection with the last mentioned test the two curves, Fig. 7, represent the result obtained with an automatic iron and with a non-automatic iron—times being plotted as abscissæ and temperatures as ordinates. Readings were taken about every 7 ½ seconds; and it will be seen that it required the automatic soldering iron but 5 1-3 minutes to reach a soldering temperature, whereas the non-automatic soldering iron required 8 ½ minutes.

In the instantaneous determination of the temperature of molten metals such as cast iron, copper, brass, and bronze, the wires at the hot end of the couple are left separated. The couple is dipped into the bath which makes an electrical contact with the two elements, completing the circuit and immediately indicating the temperature upon a suitable indicating device. When the couple has worn away to a length of about one foot, the fire end is replaced by a new one.

This form of couple with pointed ends also affords a most convenient means for determining the temperature of metallic plates, and has been used to determine the proper temperature of the plates used in the manufacture of brazing powder, and

of zinc plates in the rolling of zinc sheets. As explained, this form of couple is sometimes provided with a small, thin contact plate especially when used to determine the temperature of electrically non-conductive objects.

In a boiler test 19 couples have been applied at different parts between the furnace and the flue and connected by a proper switching device to a single indicating instrument.

From the data obtained a curve was drawn showing the temperature at all points along the path of the products of

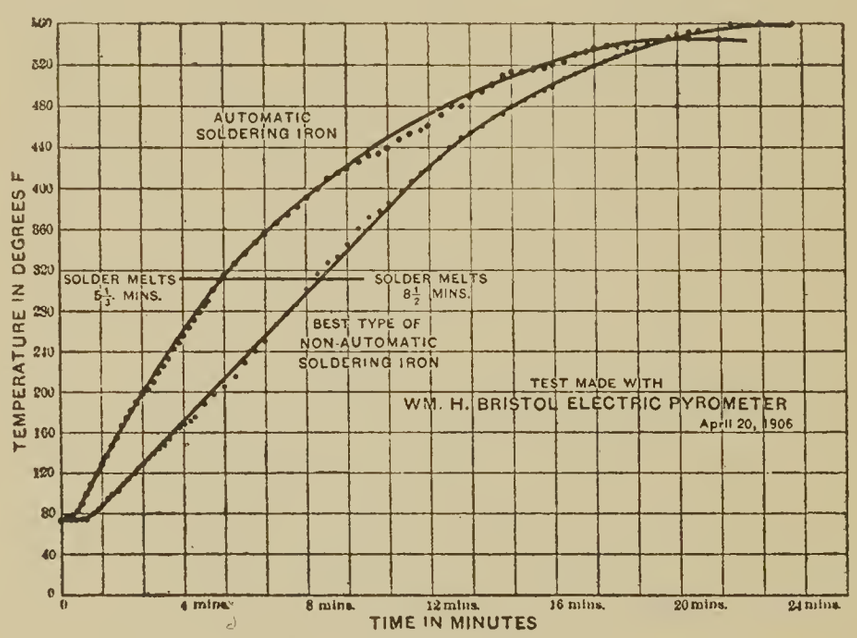



FIG. 7.

combustion from the furnace to the flue—the abscissæ corresponding to square feet of heating surface, and the ordinates to degrees Fahr.

The pyrometer has also been used to show the degree of super-heating—an indicating instrument with scale of 750° Fahr. being used.

I quote the following from the report of a recent locomotive test in which a pyrometer was used while the locomotive was running.

"In the test to-day one of the long irons, placed in the fire-box, extended in sufficient distance to catch the full force of the flames that were coming round over the arch, the iron being just at the lower end of the arch; the temperature was above 2,800° at times. About eight inches

from the back sheet we found that the temperature would be as high as 1,600°, and decreased as you approached the sheet; the temperature just inside of the sheet would average about 1,250°, of course considerable air coming up around the crown would naturally lower the temperature at this point. The smoke box temperature ranged from 480° to about 600°.

"The instrument indicates all right, and will give satisfactory results. The point quivers and vibrates very little while engine is running, a great deal less than we thought it would. At no time was it sufficient to interfere with correct reading. After connecting it up one man can stay in the cab, and within a period of about 10 seconds can read the temperature at several points in the fire-box, the boiler, ash pan and smoke box. It is simply a matter of cutting in and cutting out your switches."

In connection with its application to lead hardening baths, it has been found that not only are uniform results obtained, but that the life of the pots containing the lead is considerably prolonged due to the more careful control of temperature.

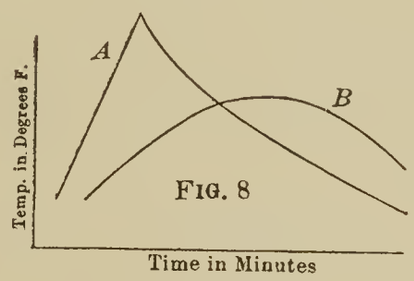


FIG. 8

The two curves (A and B), Fig. 8, show respectively the fire temperature and the temperature in the box containing the articles to be annealed—temperature being plotted as ordinates and time as abscissæ. It will be noticed that the temperature of the box rose for some time after the fire was shut down.

In the handling of many small parts such as in the manufacture of watches and clocks, a very convenient device has been constructed by a large clock company. The pot containing the articles is adapted to the hot end of the couple and the couple used as a handle for inserting the pot into the furnace or into an ordinary forge fire. By revolving the pot it is heated perfectly uniformly, and is removed as soon as the temperature is reached as shown on the indicating instrument, all guess work being thus eliminated.

The pyrometer has been successfully used both for indicating and recording the temperature of the hot blast, gas mains, and hot stoves of blast furnaces.

The thermo-electric couple has also been directly connected to a sensitive relay, which controls a local circuit or a second relay controlling a local circuit. This local circuit controls a spring, weight or motor controlled valve. The couple is inserted into a gas furnace and the primary relay set to respond to a particular temperature. This temperature may thus be automatically maintained within predetermined limits by the automatic regulation of the fuel supply.

While I have briefly outlined some of the applications of the thermo-electric pyrometer, I would say that the field for a commercial pyrometer appears very broad; but that in many cases it is necessary to educate manufacturers and the like as to the value of a pyrometer.

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## DISCUSSION.

President Hering: Before proceeding with the general discussion of these two papers, I will call on several gentlemen who are present who will contribute some information on this subject. I call Mr. R. S. Whipple, of the Cambridge Scientific Instrument Company of England.

Mr. R. S. Whipple: I should like to be allowed to express my admiration for the ingenuity shown by Prof. Bristol in overcoming the cold-junction difficulties.

I am convinced that the reason why thermo-electric thermometers have fallen into disrepute in some quarters is because the observers have not sufficiently realized that the whole of their measurements depend on the difference in temperature between the hot and cold ends of the couple. I know of a case in which, by placing the thermometer horizontally through the sides instead of vertically through the roof of the furnace, an apparent rise in temperature of 100° C. occurred. For this reason I have been urging for some time that in commercial work the cold junction should be inserted into some sort of steam bath. In nearly all works a certain amount of steam is blowing to waste and some of this, by means of a simple form of hypsometer, can be used to

maintain the cold junction at a constant temperature.

Personally, in England, we have been devoting a considerable amount of time to the development of the platinum resistance thermometer. This form of thermometer was originally suggested by Siemens, but unfortunately he made the mistake of winding his fine wire on a fire clay cylinder, which, experience has shown, affects the platinum in some peculiar way. He also made the mistake of attaching the fine wire to the heavy leads by means of a platinum screw, and I am afraid this has been the source of a large number of errors. H. L. Callendar was the first to suggest the fusing of the fine wire to the leads and also that the fine wire should be wound on a mica frame. These two important modifications, together with the addition of compensating leads, have produced an instrument capable of extreme accuracy.

You can determine any temperature ranging from that of liquid air to 1200°C with the same thermometer. It is not advisable to employ the resistance thermometer above 1,200°C.; above this temperature you must use the platinum, platinum-rhodium couple or some form of optical or radiation thermometer. The resistance thermometer is capable of extremely accurate work. Principal Griffiths, on some work on the freezing points of dilute solutions, measured differences of temperature of one-millionth of a degree Centigrade. Resistance thermometers are largely used commercially, especially for controlling the temperature of annealing furnaces. They may also be placed at a considerable distance from the reading or recording instrument.

Fig. 1 illustrates three types of resistance thermometers. The left hand one is suitable for general test work, the one in the center for very high temperatures and that on the right for annealing furnaces. The latter is fitted with a steel sheath which can be readily replaced or removed.

Fig. 2 is the reproduction of a record of the temperature of an annealing furnace. It is interesting to compare the firing of the unexperienced fireman, B, as compared with the older hand, A.

Fig. 3 shows the type of indicator generally employed with resistance thermometers. It illustrates a workman measuring the temperature of the hot air blast in a blast furnace.

The Féry Radiation Pyrometer is being exhibited. It consists

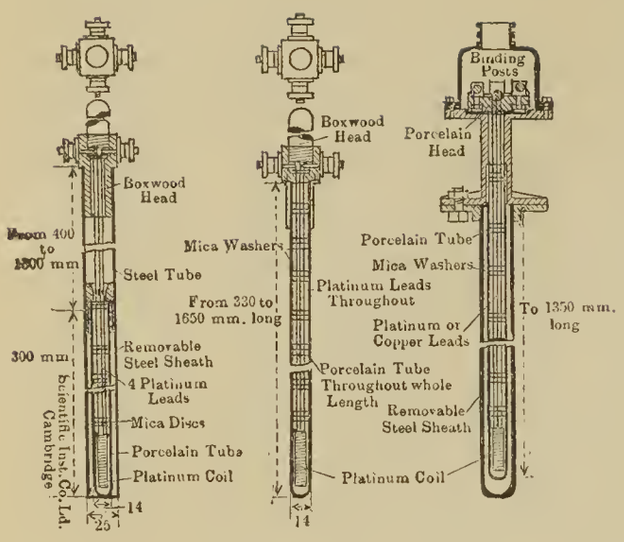



FIG. 1

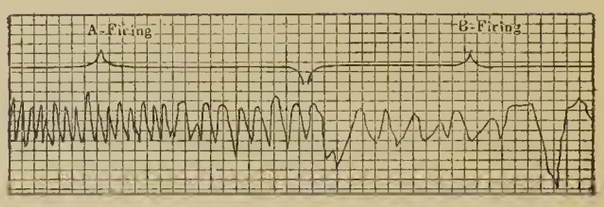



FIG. 2.

FIG. 3.

FIG. 4.

of a gilded concave mirror which concentrates the heat rays on to a small copper-constantan couple. The electromotive force generally generated is shown on a sensitive galvanometer which can be made either direct reading or recording. Fig. 4 illustrates a workman sighting the Féry Pyrometer onto a piece of work.

In conclusion, I must tell you how pleased I am to see the way in which you in America are hammering at the pyrometer question. There is a very large field and I think that your manufacturers are not as conservative as ours are in England. The English manufacturer is apt to say to the man who is trying to sell him an instrument, "Can you tell me who else is using one?" whereas the American asks, "Is it going to save me money?" and when the answer is in the affirmative he gives an order for an instrument.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 9, 1906, President Hering in the chair.*

## THE HERAEUS "LE CHATELIER PYROMETER."

By Dr. R. Moldenke.

The Le Chatelier Pyrometer is the instrument which all men of scientific attainments recognize as having given the world a ready means of correctly reading temperatures up to about 3,000 degrees F., both in the laboratory and in connection with industrial processes.

The measurement by a sensitive galvanometer of the very feeble current caused by heating the junction of two different metals, or alloys, was carefully studied by Prof. Le Chatelier, who discovered that the combination of pure platinum with an alloy of platinum with 10 per cent. rhodium would give results entirely reliable, and free from the annoying parasite currents developed when other metals or alloys were employed. The result was the now well-known instrument, and the purpose of the few remarks to follow is to explain the several points which make the instrument, as brought out by the firm Heraeus—(Hanau, Germany), peculiarly deserving of attention.

When the Le Chatelier pyrometer was first brought to the attention of the scientific public, and its excellencies were realized, the German Government, through its Physicalische Reichanstalt, of Berlin, undertook to determine the proper length, thickness, and resistance, of the couple which would give the best results, and could therefore be made standard. This was found to be a length of 58 inches, a diameter of the wire of No. 23 B. and S. gauge, and a resistance of 1.6 Ohms. To get as near perfection in the preparation of the element as possible, the work of preparation was entrusted to Dr. W. C. Heraeus, the proprietor of the platinum works of that name.

Dr. Heraeus, in working out the problem of supplying a couple which would be absolutely uniform and interchangeable

at all times, provided two blocks of the necessary materials worked up to uniformity in structure and perfectly pure. Thus there is available a supply that will last far beyond a life-time, and the first as well as the last couple is absolutely the same. This feature alone makes the pyrometer a true standard and saves the busy engineer of to-day all thought of adjustment, recalibration, interchangeable arrangements, and the like time-consuming troubles. Some of the instruments were in use ten years and are as good as when first applied.

In its essential form, the Le Chatelier pyrometer is a thermo-couple, the free ends of which are connected to the terminals of the galvanometer coil. Heating the junction of the two wires of the thermo-couple causes the formation of a feeble current, which, flowing through the armature of the galvanometer, turns it in the field of the permanent magnet. A pointer connected to this indicates the electromotive force in millivolts and by careful calibration the temperature on a graduated scale. It will be readily seen that this exceedingly simple arrangement, if properly guarded by first class apparatus, should be easily understood and handled by ordinarily intelligent men, once they are shown how to use it. Indeed, my personal experience with the instrument in daily use in the Malleable Cast Iron foundry, where the temperature of the annealing ovens has to be taken regularly, and where a small fortune is at stake continually, bears this out fully, an ordinary laborer selected for trustworthiness recording the temperatures observed for the benefit of the annealer in charge. The ease with which the instrument is applied in the particular case in point is shown by the fact that where formerly the Siemens' Water pyrometer occupied the attention of two men in the twenty-four hours, with the Le Chatelier pyrometer, the galvanometer located centrally, and the ovens wired up, the thermo-couple is introduced into the oven, and while the man walks to the galvanometer the pointer has reached the stationary point, the reading is taken, the thermo-couple moved to the next oven, and so on. A few hours in the twenty-four is all that is required, and the results are accurate easily within twenty-five degrees F. Parenthetically, it may be said that the temperature of the coldest pot of the annealing

oven for annealing malleable castings should not fall below 1,250 degrees F., nor go above 1,350, this for the best results with fairly heavy castings and on furnace iron. What sins have been committed before a good pyrometer was available can be better imagined than described. Again when I made the series of determinations of melting points of cast iron, and traced the connection of the combined carbon content with the melting point in regular succession, I found this instrument invaluable, especially for its heavy wires and the consequent amount of punishment it would stand in such an investigation.

An important point in using the Le Chatelier pyrometer is the care of the connection between the free ends of the thermo-couple and the copper leads to the galvanometer. Theoretically, they should be placed in melting ice. In commercial work, however, the slight variation may be safely ignored, whereas for scientific research, greater care must be taken. The thermo-couple is encased in a porcelain tube where this can be heated up gradually so as not to crack. For taking the temperature of molten metals, a clay tip arrangement is essential, as this can be dipped into the ladles directly without injury, and the temperature observed within a half minute or so. There is no end of uses for this pyrometer. I remember examining the temperatures existing in an open hearth glass pot furnace, where much difficulty had been experienced with the product on account of excessive variations of temperature due to inability to regulate the heat in the absence of the necessary knowledge. The place for the thermo-couple was finally located in a protected place in the furnace, but it was interesting to note the effect of little cracks in the silica brick crown, where the introduction of a slight current of air gave rise to a combustion which melted off the couple as fast as it was lowered in. As a result greater care was taken with the furnaces, and better glass made.

The study as well as the application of the heat treatment of steel furnishes a most interesting field for the Le Chatelier pyrometer, without which we would not be as far advanced as we are. Chemical works, plants making refractories, potteries, etc., the electrical industry, in fact, but few industries in which

heat is made use of can afford to be without a reliable pyrometer. Even the boiler room can come in for a share of attention. I remember having to solve the smoke problem in our plant in Pittsburgh, at one time, and only after applying the Le Chatelier pyrometer to every possible place in the 1,000 horsepower installation, did I find the solution. The breeching and base of the stacks gave entirely too high temperatures for proper economy. An investigation of the grates showed that they were burned out too often. Smoke poured from the stacks of the overworked boilers, and these had to be kept going at full pressure night and day. The stacks were raised an extra fifty feet, one by one, making 150 feet in height each. The coal now danced on the grates. Plenty of oxygen got at the fuel. The grates did not burn out after this, and the boilers gave full value and over without a particle of smoke. Here was a case where the best of stokers, a coal conveying system, and ash removal, were installed with the highest class of water-tube boilers, and yet the overcrowding which always takes place in a live growing works brought a lot of trouble, quickly solved when the pyrometer was applied. There are others who might profit by doing this at their plants.

The galvanometers used in connection with the Heraeus "Le Chatelier" pyrometer are of the d'Arsonval type, and are specially adapted to the measurement of these very feeble currents. They are made by the well-known firms of Siemens, and by Hartmann & Braun, and, therefore, need no further comment beyond mentioning that they can also be obtained of the recording type.

Just a little gossip in concluding. The Jury of Awards of the St. Louis Exposition, on which I had the honor to serve, in giving Mr. Engelhardt, the American representative of the Heraeus Le Chatelier pyrometer, a gold medal for his exhibit, and especially the introduction in large quantities of this useful instrument into this country to its lasting betterment industrially, regretted that Prof. Le Chatelier had not made a personal exhibit, so that they could award it the Grand Prix. Could a better recommendation be given any instrument when a committee of nearly all civilized nations informally gave expression to such a thought.

*(A Price thermo-electric pyrometer, made by the Electric Dental Supply Co., Cleveland, Ohio, was exhibited, and the following description of it was given.)*

Two couples are shown in connection with the instrument, for demonstration purposes, but out of the some 125 different industries which are now using this type of pyrometer, very few have the same kind of couples, since the material of the wires, and also their length and size in the couples, depend upon the conditions of the several industries in which the instrument is to be used. For high temperatures, platinum is required, in order to get reliable results, but for low temperatures, other metals are equally good.

The two wires of the couple are insulated from one another in several different ways. Where compactness is of importance, they may be run through magnesia, ⅛-inch outside diameter, and having an 18 B. & S. hole. Another way is to secure clay tubes sufficiently refractory to stand high temperatures, having holes pierced through from end to end. Sometimes, the wires may be held apart by asbestos cord, woven in and out; asbestos tubing is excellent where there is a great deal of vibration.

For higher temperatures, which reach about 1,600° C., or more, it is necessary to use a refractory or semi-clay porcelain tube which is closed at one end, unless very sudden changes of temperature are to be recorded, when the end of the couple or junction is run outside. It is still better if these tubes are glazed on the outside, to prevent any possibility of contamination to the thermo-couple by furnace gases.

Where the heat is extreme, these tubes are often again supported by large fire-clay tubes, to project through a short distance. This prevents the sagging of the porcelain tube when it is in a horizontal position, and also prevents it from breaking. When inserted in a clay tube, it has been found to last three or four times as long.

When working at higher temperatures with platinum, iridium and rhodium, it has been found better to use two couples in series, in order to get greater precision or accurateness of temperature. In this case, the cold end of the couple need not extend far from the hot one, but may be joined there by certain wires of a

metal, which develops a counter electromotive force, equal to that set up by the cold junction. This has been perfected to a high state of efficiency, allowing, in some cases, the cold end of the couple to be at temperatures as high as 500°C., thus greatly reducing the length of the couple. But at temperatures less than 850° or 900°, there are several metals that may be used and can be relied upon. Brass and alloy of copper and nickel gives a very high and steady e. m. f. Iron used with the same alloy is almost as good, unless it is exposed to injurious furnace gases.

The method used in the Price pyrometer for its indicating instrument, is to suspend the armature on one single point, since when an armature is suspended between two points, and turned over, sometimes in a horizontal position, it is bound to cause a considerable amount of friction, which consequently prevents accurate reading of temperatures.

The incoming leads to the armature are crimped suspension springs extending 4 or 5 inches above the armature. Where they are attached, the inlets to the armature are very close together, but the ends at the top are further apart, to give the proper torsion and resistance to the current. The crimp in these springs allows a lengthwise spring of nearly ¼ inch in that distance.

When the armature is suspended in its place above the point, a large proportion of its weight is carried by these suspension springs, and only enough is left on the point to keep it centered around the core and in the field. This reduces its internal friction to almost nothing, making it possible to get movement distance, so that it is almost impossible to break them.

The thermo-electric pyrometer can readily be arranged to give a continuous record of temperature. At every minute, a tiny spark leaps from the indicating needle and passes through a continuous sheet of paper to a contact below. This paper has marked upon it the hours, and parallel lines representing the temperature. It is just as easy to see the temperature on this recording instrument as on the ordinary indicating instrument, as the paper underneath the needle, leaves the ordinary scale in view just the same as usual. It has the advantage that it has no inclination whatever to retard the needle, but allows it to show the exact measure of the temperature, both on the scale and the hole through the paper.

These holes appear similar to the puncture of a pin. One of these recording instruments may be in a head office, and it may be a single, double, or triple machine, recording the temperature of one, two or three places at once, while at the plant, for the use of the fireman, is an indicating instrument connected to the same couple or couples as that used by the recording instrument, so that the fireman always sees just the same temperatures that the recorder is continuously marking. The wire connecting the couple with the galvanometer may even be a mile in length.

For the calibration of these instruments, fixed points are, of course, required. Copper melted in a graphite crucible, with its surface protected with powdered graphite, gives a very definite and sharp fixed point at 1,084°C. when freezing (Day and Allen's value is 1,083.6°, in a reducing atmosphere). During the freezing period, the temperature remains quite constant, giving ample time for observations. Certain grades of gold in a very loose form, or rolled exceedingly thin and bunched up in a small bunch, will usually melt within 5°.

The instrument is very well adapted for immersion in small specimens of steel and other metals, for the study of the cooling curves, and in connection with annealing, hardening, etc.

While thermo-electric pyrometers were formerly used almost exclusively for high temperatures only, the Price pyrometer is now also made to give temperatures below, as well as above the freezing point of water. When the outside junction is carefully wrapped in wool of sufficient thickness, in order to maintain the temperature uniform (wool being supposed to be the best non-conductor of heat that we have, being five times as efficient as asbestos), a very reliable instrument can be made to show the temperature from 50° below zero to the boiling point of water.

## DISCUSSION.

Mr. Brown: We manufacture a number of different types of pyrometers, but I thought it would be best to bring over two that possibly some of the members of the society may not have seen. These pyrometers are of rather a novel type. It is a platinum instrument, the essential feature of which is a thin strip of platinum hung between heavy iron frames. When the stem of the instrument is inserted into the heat, the thin platinum strip quickly heats up to the temperature of the surrounding atmosphere, whilst the heavy iron frame is very slow to heat up. The platinum strip is directly connected to the pointer on dial, through a multiplying movement. As the platinum strip is instantly heated in the gas or air, the temperature of which we can call 2,600°F., the pointer passes around the dial, due to the expansion of the platinum strip. When the platinum strip has attained the temperature of the surrounding gas, it will have reached its maximum expansion for that degree of temperature. The pointer will then cease its movement. Meanwhile the heavy iron frame holding the platinum, which has only risen in temperature to possibly 200° F., continues to expand as it heats up, and begins to pull the pointer back, after the platinum has ceased expanding. Before the pointer starts to return, the temperature is noted, and the pyrometer withdrawn. As each instrument is standardized separately, the temperature as indicated on the dial, is the correct temperature of the heated gas. Possibly I may have an opportunity to show you how the instrument works, by means of one of these burners.

This is a recording pyrometer consisting of a tube enclosing graphite rods, and the recording case to which the tube is fastened. The graphite rods are connected to the movement in the case, by a compensating rod, compensating for various depths of immersion of the tube, inserted into the heated gas or metal. The indication of the temperature is caused by the expansion of the steel tube, and the non-expansion of the graphite rods. This recording pyrometer is for use up to 1,500°F., and the platinum pyrometer, previously described, to 3,000°F.

I have several records from the recording pyrometer here. One of these records was made by this pyrometer in use on the gas main or downcommer at a blast furnace, and may be of interest. When the pyrometer is inserted in the heat, the platinum strip will be totally heated in 15 seconds. The pyrometer is then withdrawn from the heat. Before using it again it is necessary that it shall be allowed to cool down to the temperature of the atmosphere of the room, which takes about 15 or 20 minutes. The condition of the platinum strip has little chance to become altered with continual use, as it is subjected to the high temperature for less than 15 seconds at a test. The quick acting platinum pyrometer, as it is known, is chiefly used for measuring very high temperatures.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, October 9, 1906, President Hering in chair.*

# THE DECKER PRIMARY BATTERY.

By Professor Francis B. Crocker.

On May 16, 1888, the writer read before the American Institute of Electrical Engineers a paper on "The Possibilities and Limitations of Chemical Generators of Electricity." This paper discussed and compared the various types of primary cells. It was shown that about one pound of zinc and a few pounds of other materials were capable of producing a horse-power hour of electrical energy, and the statement was made that "the possibilities are very,very great." On the other hand, little or no progress had been made with the primary battery for almost a half century, so that the outlook was discouraging, especially in regard to its structure and handling. Hence the conclusion was reached that "the *apparatus* is at fault, not the *chemical action*" (italics in the original). Let us consider briefly the principal historical facts.

The original form of primary battery, or "couronne de tasses," which was the first known source of electric *current* in contradistinction to static *charge,* was invented by Volta in 1800. Amalgamation of the zinc was introduced by Sturgeon in 1830. The two-fluid type of primary cell with porous cup to separate the fluids was invented by Daniell, in 1836. The use of nitric acid as an electronegative fluid or "depolarizer" more powerful than the copper sulphate of the Daniell battery, was due to Grove, and dates from the same year (1836). In the Grove cell a platinum negative plate is employed to withstand the action of the nitric acid, and Bunsen in 1842 substituted carbon for this expensive metal. Poggendorff, in 1842, devised a single-fluid cell in which a solution of potassium bichromate mixed with sulphuric acid was used as a depolarizer instead of the nitric acid of Grove, thereby avoiding the obnoxious fumes without material sacrifice of power. One is at a loss to point out any

radical or even important advance in primary batteries since the time of these fundamental improvements. In other words, so far as the types now on the market are concerned, they are not substantially better than what might have been obtained more than sixty years ago. This is all the more remarkable when it is remembered that practically all the modern applications of electricity, with the exception of the telegraph, have been made since 1876, a period only one-half as long, during which the dynamo-electric generator has been developed from one horse-power to ten thousand, its efficiency and mechanical construction being vastly improved at the same time. It should be noted that the Leclanché cell (with sal ammoniac solution) was brought out in 1863 and the so-called "dry" batteries about 20 years ago; but these types are applicable only to intermittent service, such as ringing electric bells, and even for short periods are incapable of giving any considerable electric power. Hence they constitute a special class adapted to perform merely light duties, and should not be included or compared with batteries capable of operating electric lights and motors. The Lalande battery was invented in 1881, and is now manufactured and used to supply considerable amounts of electric power, in fact, it is practically the only type of primary cell employed to any extent for this purpose. Definite statements and figures in regard to this battery will be given later.

The quotation from the writer's paper in 1888, to the effect that "the *apparatus* is at fault, not the *chemical action*," applies equally well to the primary battery of 1906 so far as any types now upon the market are concerned. They usually consist of separate glass or porcelain jars, clumsy and liable to breakage; electrical connections are made by wires and binding posts, inconvenient and exposed to corrosion as well as to mechanical injury; with no way to supply fresh liquids except by the laborious and sloppy process of pouring them into each cell separately. A picture of a primary battery in 1850 compared with one of 1906, would show little difference in favor of the latter, certainly nothing radical. On the other hand, compare a dynamo of 1878 with one of 1906, an interval exactly half as long! This Chinese progress of the primary battery which was discouraging in 1888 became more so as time went on, and the opinion of the writer, if

expressed in 1904, would not have been much more favorable than in 1888, since there was little or nothing upon which to base hope of material advance in this direction. The principal weak points of the primary battery are first, high internal resistance limiting its power and efficiency; second, weakness and looseness of its parts exposing them to breakage or derangement; third, exposure of the electrical connections to corrosion as well as to mechanical injury; fourth, the great inconvenience and the likelihood of spilling the liquids when a battery is being emptied of an old charge or supplied with a new one; fifth, the high cost of the materials as well as labor required for recharging. Practically none of these five difficulties has been overcome or even mitigated, so far as published information goes. Recently, however, it has been the writer's good fortune to examine and test a primary battery in which the first four of these defects are actually overcome and there is good prospect that the fifth will be largely reduced.

## CONSTRUCTION AND OPERATION.

The battery to which I refer has been developed during the last two or three years by Mr. F. A. Decker of Philadelphia. It is of the two-fluid type with zinc plates immersed in dilute sulphuric acid and graphite plates in a solution of sodium bichromate and sulphuric acid. The materials and chemical action are, therefore, similar to those of other batteries, the original features being found in the *construction* of the parts and the manner in which they are put together. The size and number of plates employed in each cell depends upon the current required, but ordinarily there are two or three flat zinc plates about 5½ inches wide by 9½ inches high, each weighing about 1 lb. Each zinc plate and the dilute sulphuric acid surrounding it are contained in a flat porous cup. In order to form such a cup two unglazed earthenware plates with thickened edges and diagonal strengthening ribs are shaped separately in steel moulds, a special clay mixture being employed to obtain any desired porosity. These plates are made extra thick to prevent warping in burning and produce true, flat surfaces and straight edges. They are then united to form a flat cup, after which it is ground down on each surface to the desired thinness. In point of fact,

the finished walls are very thin, so that light will show through them, which enables the degree of uniformity of thinness to be readily determined. The grinding operation involves little time or skill, being performed by half-grown boys. In this way a flat porous cup is obtained perfectly true on all sides and with walls much thinner than could possibly be made if it were attempted to form a complete cup in the first place. At the same time, this cup is amply strong, no breakage being found to occur even in automobile service. Two of these porous cups, PP, are shown in Fig. 1, in combination with three graphite

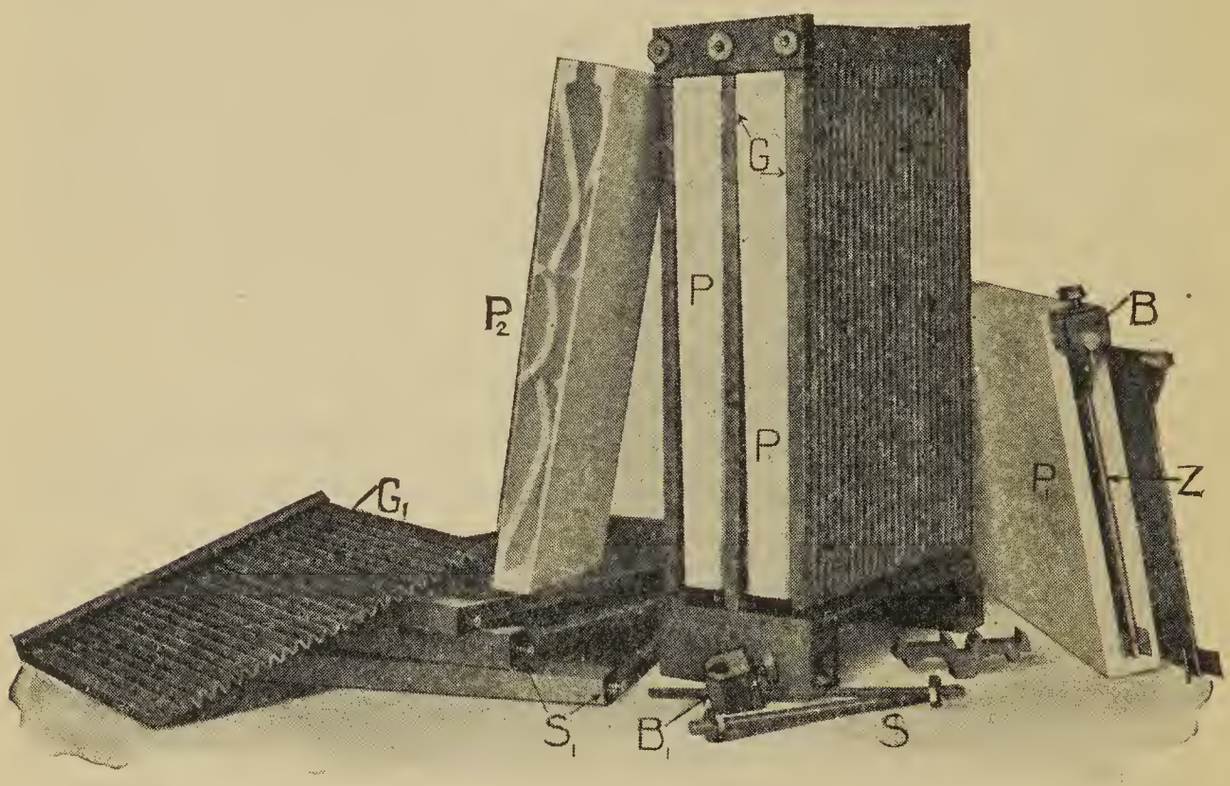



Fig. 1.

plates, G G G, and at P, with a zinc plate Z, also one of these porous cups sawed through vertically is seen at $P_2$, the strengthening ribs on the interior surfaces as well as the thickened edges being visible. The exceeding thinness of the walls of these cups tends to reduce the internal resistance to a minimum for any two-fluid cell, and the fact that these walls are true, permits the graphite and zinc plates to be placed close together, also tendency to minimize the resistance. By actual test it is only .013 ohms for a cell of the kind described with two zinc and three graphite plates, all connections and the resistance of the plates themselves being included.

The negative plates are of graphite, being corrugated so as to offer large surface for the free action of the depolarizer; being also provided with thickened edges and diagonal ribs to give them strength as well as to decrease their electrical resistance. Three of these plates are represented at G G G, in Fig. 1, as already stated, and half of another is seen at $G_1$, having been sawed in two to show the corrugation.

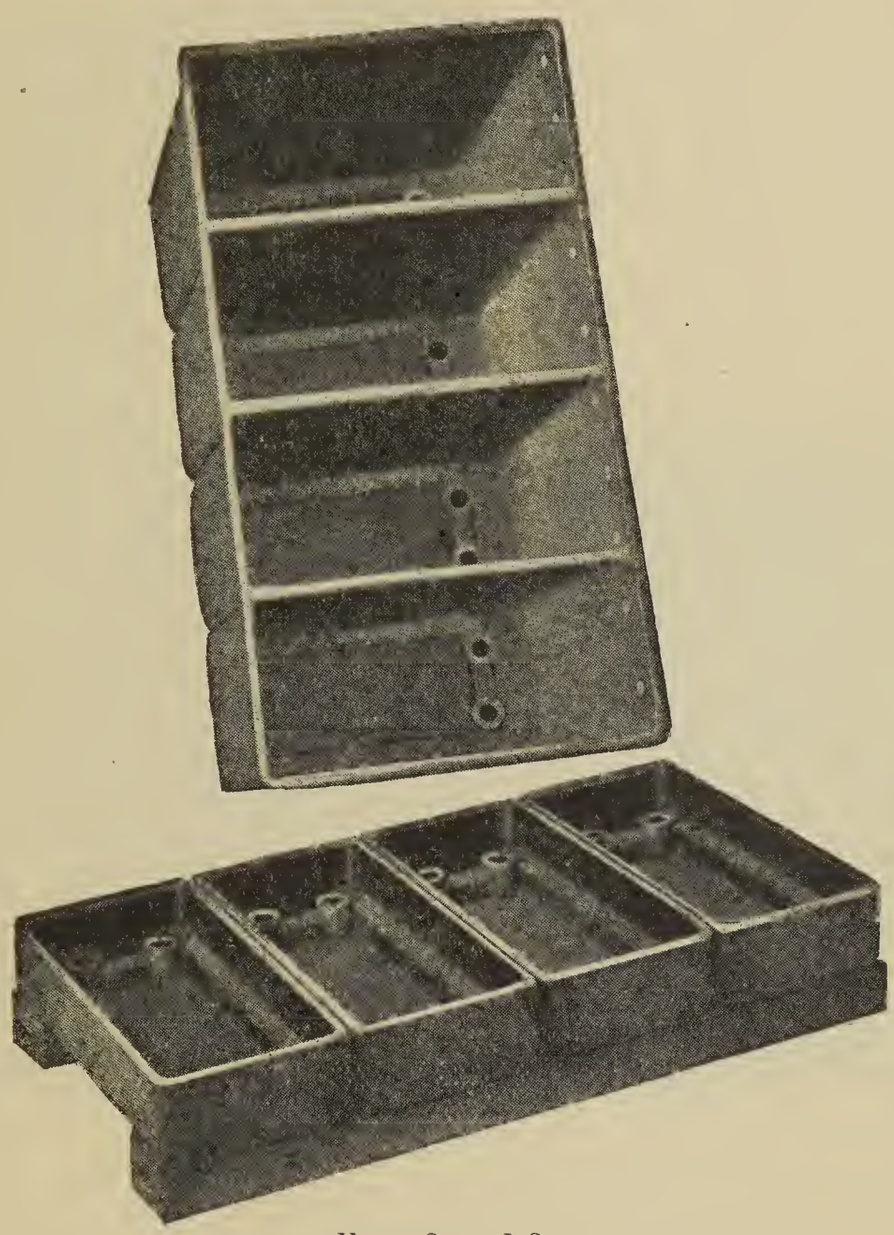
The space around the porous cups and graphite plates is filled with the depolarizer consisting of a solution of sodium bichromate mixed with sulphuric acid which is introduced into the containing vessel of hard rubber as explained later. One of these vessels comprising four cells is shown in Fig. 2. In order to assemble a battery, the two porous cups, P P, in Fig. 1, each containing a zinc plate, with the three graphite plates G G G, are placed in one of the cells of the containing vessel in Fig 2, other similar sets being put in the other cells. To supply dilute sulphuric acid to the porous cups each one communicates through a small opening at the bottom, with a conduit in the base of the containing vessel. The two outlets of this conduit in each cell are shown in the bottom of the containing vessel in Fig. 2. The openings of the two porous cups are respectively connected to these outlets by means of vulcanized joints free from leakage or acid action. The conduits leading to the various cells are branches from the main conduit that extends the entire length of the containing vessel under one side. The depolarizing fluid is supplied by a similar set of conduits, but, in this case, it is sufficient to have one simple outlet in each cell. It is objectionable to have direct electrical connection between the various cells through the liquid contained in these conduits because a certain short-circuiting or leakage of current would occur. This is reduced to an insignificant amount in the Decker Battery by making the branch conduits of considerable length and small cross section. A containing vessel of four cells with the upper part cut off is shown in Fig. 3. The two outlets in each cell which supply the two porous cups with dilute acid are connected to the main conduit, C, by a branch conduit extending across the cell. Similarly the outlet that feeds each cell with depolarizer is connected by a branch conduit to the main conduit, $C_1$, on the other side. In this way the total length of the

liquid connection between the cells is made very considerable. The main and branch conduits with their connections to each other and to the cells and porous cups are composed of hard rubber all vulcanized together, forming what has been aptly called an irrigation or drainage system since it performs both functions. The several cells that make up the containing vessel in Fig. 2 are also vulcanized together, so that the complete battery with all its cells, conduits and porous cups constitute one substantially integral mass with no loose joints or parts. The graphite and zinc plates as well as their connections are also held very firmly in place so that the battery, as a whole, may properly be claimed to be an integral structure or unit.

The electrical connections in batteries have always been a source of much trouble, being difficult to make and still more difficult to maintain because of the corrosive action of the liquids. In the Decker battery the connection to each graphite plate is made by a brass screw extending several inches into its thickened upper edge. One of these screws is shown at S, in Fig. 1, and the end of another is seen projecting from a carbon plate at $S_1$. When the plate is in place, this end of the screw passes out through a hole near the top of the containing vessel, being held firmly by a nut on the outside. The connection to the zinc plate is made by means of a long tapering zinc plug inserted in a zinc block, B, and $B_1$, in Fig. 1, enabling the plate to be readily renewed, at the same time making a good mechanical as well as electrical joint. This zinc block is held in place by a screw passing through the wall of the containing vessel with its head outside. The carbons of one cell are connected together and to the zincs of the next cell by a brass strip placed under the nuts and heads of the screws. We see, therefore, that connection is made to the graphite plate (impregnated with paraffin along its upper edge to make it impervious) by a long screw embedded in it, and giving extended contact surface. The zinc plate, plug and block being all of the same material are free from voltaic action, and all the rest of the connections, including those between the plates of each cell as well as between the cells, are *external* to the containing vessel. Hence all trouble is avoided from corrosion, loose connections or poor contacts of any kind; this statement being borne out by experi-

ence. It is this care as to correctness of design and perfection of details that frees this type from the serious defects in structure and operation that have characterized primary batteries for 106 years.

The two fluids are caused to run into, or out of, the battery by connecting the two main conduits, C $C_1$, (Fig. 3) already



FIGS. 2. and 3.

described, with two supply tanks by means of rubber or lead pipes, each main conduit being provided with a socket or nipple to which the pipe is attached. The fluids may be caused to flow by a pump or siphon, or by raising and lowering the supply tanks, thereby driving the liquids into the battery, allowing them to run back by gravity. This is the arrangement represented

in Fig. 4, a battery of 16 cells, being supplied from two tanks below. The switch above, on the right, not only closes the circuit and lights lamps, for example, but also turns air pressure into the tanks thus filling the battery. The large cell on the floor to the right is a type having 10 zinc and 11 graphite plates, being capable of giving 120 amperes, for 6 hours, at an average

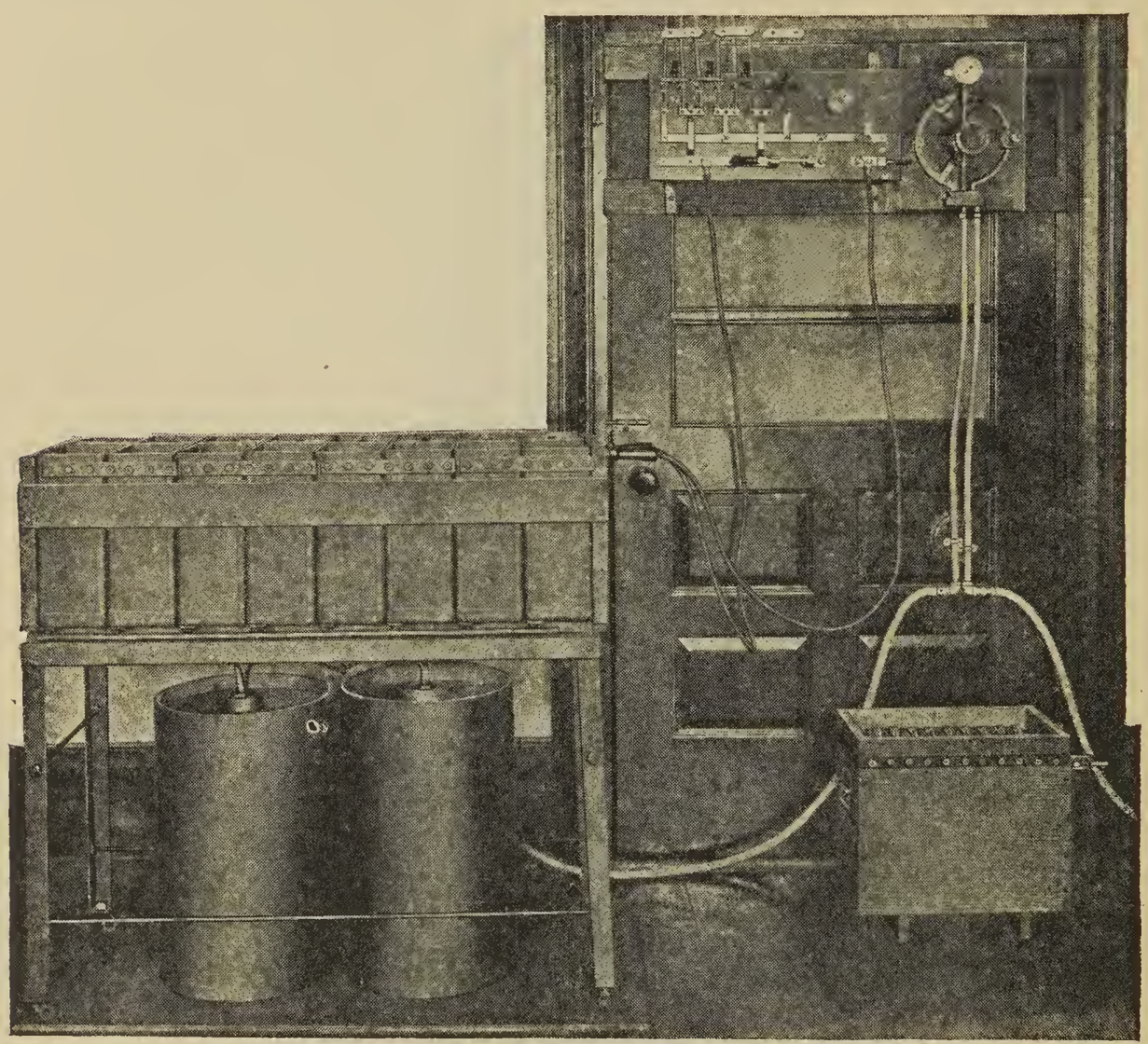


FIG. 4.

of 1.7 volts. It is intended for heavy work, having a lead-lined, containing vessel of wood.

## RESULTS.

The results obtainable from the Decker battery are shown by tests made personally by the writer. A cell of the form described, having two zinc and three graphite plates, was discharged for a period of 5¼ hours at 24 amperes, the external potential

falling from 1.9 to 1.3 volts. In other words, the cell gave 126 ampere-hours at an average voltage of 1.73, or 218 watt-hours. The cell was then shaken so as to stir the liquid and gave 24 amperes for 53 minutes longer. This corresponds to the condition that would exist in electric vehicles, boats and train lighting. The total output, therefore, was 147 ampere-hours at 1.684 average voltage, or 247.55 watt-hours. As the complete cell weighed 16 lbs. 14 oz., including all solutions, connections, etc., the output was 14.7 watt-hours per lb. of total weight, which is an output about twice as great as that obtained from the standard types of storage battery now manufactured and used. To put these figures in simple form for ordinary business purposes, it may be stated that a cell weighing 17 lbs. gives 150 ampere-hours at an average of about 1.7 volts, or about 250 watt-hours, which is equivalent to one-third of a horse-power-hour. The output is nearly 15 watt-hours per lb. of complete cell.

In this connection it should be remembered, however, that the liquid constitutes only about one-half the total weight of the battery, hence it would be possible to carry in tanks an additional amount of solution equal to the weight of the battery, in which case we could obtain three times as much electrical energy with only twice the total weight. In other words, the output would be 22.5 watt-hours per lb., which is about three times that obtainable from a standard storage battery. It would not be necessary to renew the zincs because they are sufficiently thick to be equivalent to three or more charges of liquid.

A second advantage of the Decker battery compared with the storage battery in addition to this large saving in weight is the facility of recharging it by simply running out the liquids and refilling with fresh solutions, which can be done in less than five or ten minutes compared with five hours or more required by recharging a storage battery.

A third advantage of the primary battery is the fact that it has no limit in voltage beyond which the discharge cannot safely be carried. If desired it can be discharged indefinitely until there is practically no power left. In the case of the storage battery on the other hand, it is very objectionable to discharge below 1.6 volts per cell on account of the danger of "sulphating" and serious injury to the plates.

A fourth advantage of the primary type is the fact that it is not necessary to recharge it immediately after the discharge, whereas, is is decidedly objectionable to leave a storage battery in a discharged state for any length of time.

The principal, if not the only disadvantage to be considered, in comparing the Decker battery with the storage battery, is the rather high cost of recharging the former.

### COST OF OPERATION.

The weight of zinc, sulphuric acid and sodium bichromate required to give 1 horse-power-hour in the Decker battery, assuming all materials to be thrown away after being used once, would cost about 35 cents, which is a high rate. It should be remembered, however, that the several important advantages which have been pointed out, will offset this item for many purposes and in many places. It would be absurd, of course, to claim that any primary battery can compete directly with the dynamo driven by steam, gas or water power where such a source is available. There are applications, however, for which it is not practicable or convenient, and these will be set forth later. Furthermore, the first cost of the battery is not high and its depreciation is very small. It is expected, also, that the cost of the materials required for recharging will be much reduced by recovering or regenerating them. That is to say, the liquids drawn off from the battery after it is discharged are treated electrolytically in suitable cells to regain the zinc and reoxidize the chrome solution. In this way, there would be very little actual loss of materials, and the cost of operation per horse-power-hour would be simply the cost of the electrical energy required for regenerating the materials plus the labor involved. The latter would not be great because the liquids could be transported in the tanks in which they are sent out and can be caused to flow through pipes into or out of electrolytic cells. In this way, the operation of recharging this primary battery would not cost much more than recharging a storage battery. The only real difference in principle between the two cases is the fact that the charging, or regeneration and discharging of the former, take place in different cells; whereas, both operations are performed in the same storage cell. So far as transportation is concerned the primary battery would have decided advantages:

First, because tanks of liquid are much more easily portable than storage batteries, and second, the liquid for the primary battery weighs only one-quarter as much as an equivalent storage battery which must be carried as a whole, or say one-third as much, including weight of tanks. The recovery process has been experimented upon with encouraging results.

## APPLICATIONS.

An electric vehicle cannot be connected with a dynamo except through a trolley wire or third rail. Where such connection is not feasible, as in the case of cabs, pleasure vehicles, trucks, delivery wagons, etc., the only electrical source of power now available is the storage battery. The advantages of the Decker compared with the storage battery have already been set forth and they are certainly very substantial. The higher cost of the electrical energy which is the only disadvantage of the former, would probably be a small matter in many cases. The other items of expense in operating an electric vehicle or gasoline automobile are so high, for example, the cost of tires, that a little higher rate for electrical energy would often be insignificant or more than overcome by advantages gained. Furthermore, the depreciation of a storage battery is much greater than that of the Decker battery: Assume a vehicle storage battery to have a life of 5,000 miles, after which the renewals would cost at least $120, or 2.4 cents per mile, being more than the cost of the electrical energy at 10 cents per kw hour. Hence several of these incidental items are higher than the cost of the energy itself. What has been said in regard to the electric vehicle would apply to electric boats, the general conditions of service being similar.

For the purpose of lighting railway trains, the advantages of the Decker battery already explained would all apply. In fact it seems that this application is one of the most favorable of the various possible uses to which this battery may be put. The equipments could be much more easily applied to the cars than is possible with the electric generator and storage battery combinations now used, it being sufficient merely to carry the battery and tanks of liquid, and not necessary to attach and connect electrical generators or other machinery. Furthermore, the power is obtained without any drain upon the power of the

locomotive which is sometimes taxed to its utmost with a heavy train and steep grades.

There are also many places in the country where it is either not possible, or not convenient, to obtain electrical energy by direct wires from a central station or electrical generating plant; in such cases this primary battery would afford a simple and convenient source of supply. Electric lights for reading and for sick rooms, electric fans, advertising lights and devices, dental motors and many other pieces of electrical apparatus may be operated in this way. The cost of electrical energy with regenerating of the materials would not be much, if any, greater than the rates charged by electric lighting companies in some of the smaller towns.

The Lalande type is the only primary battery now on the market from which any considerable current in amperes or power in watts can be obtained. One of these cells having approximately the same total watt-hour capacity as the Decker cell described, weighs 25 lbs. compared with 17 lbs. It is not practicable, however, to discharge it at even one-eighth the rate in watts obtainable from the Decker cell, the latter weighing only about two-thirds as much. It is also a fact that the voltage of the Lalande type when giving considerable current is very low, falling to .3 or .4 volts with currents of 10 or 12 amperes, whereas, the Decker cell weighing only 17 instead of 25 lbs. gives 24 amperes at 1.9 volts initial and 1.7 volts average.

One might think that at 35 cents per horse-power-hour, the cost of energy given for the Decker cell would be prohibitive, but, nevertheless, the cost of about five dollars and thirty cents ($5.30) for the same amount of energy for cells of the Lalande type has not been found prohibitive, since batteries of this class have been, and are being used in large numbers.

It is evident from the statement of facts contained in this paper that Mr. Decker has made a remarkable advance in the primary battery art.

## DISCUSSION.

MR. SPERRY: I would like to ask about those weights. How much of the battery weighs seventeen pounds?

PROF. CROKER: One cell. These three cells would therefore weigh fifty-one pounds complete with solution. The cell I tested that gives one-third of a horse power-hour weighs a little less than seventeen pounds. These cells may be different. The same proportion would hold true.

MR. SPERRY: What part of the additional plant ought we to include as the operating weight? Your photograph includes quite a plant other than what we have on the desk there. How much of that ought to be included?

PROF. CROCKER: You have got to have two supply tanks and could run in the liquids through a rubber tube.

MR. SPERRY: Have you the curve of discharge at different rates?

PROF. CROCKER: No.

MR. SPERRY: I should think these would be essential.

PROF. CROCKER: It is fully as constant in voltage as a storage battery.

MR. SPERRY: Then its voltage would be seventeen-twentieths of that of the storage cell.

PROF. CROCKER: The average voltage for the total discharge carefully calculated from the discharge curve was 1.7.

MR. SPERRY: Has any test been made on the rough usage?

PROF. CROCKER: Yes, it has been used on an automobile.

MR. SPERRY: It seems that those graphite plates are rather fragile.

PROF. CROCKER: I do not think they are. They have thickened edges and the corrugation tends to make them stronger than the same weight of plate not corrugated.

MR. SPERRY: You haven't put it in actual use, on a beer truck for instance, and severe tests of that kind run over rough pavements?

PROF. CROCKER: It has been operated in an automobile and in one case the automobile got away from its driver, and ran up on the sidewalk and into a fence. It was not intended to make that test, but it did happen. The battery was not injured, although

the machine ran over a granite curb and into a fence, and the vehicle itself was considerably injured.

Mr. F. A. Decker: Regarding the question you have just asked, Mr. Sperry, I would say that in the past two years, in all kinds of weather, we have tested this battery and made every attempt to discover its weak points. We have not found it necessary to make any great changes regarding the structure of the cells, or reinforcement to the porous cups.

Regarding the first question you asked, as to the additional weight to the battery of the lead tubes used in filling, we will imagine we have a battery of 30 cells. The size of the tubes will vary with the number of cells in the battery to be filled. To fill a battery of 30 cells the tubes would probably weigh about a pound, This would mean that the additional weight chargeable to each cell would be very small.

Mr. Sperry: I did not understand that all those were coupled up.

Mr. Decker: It would be very inconvenient to bring here ten or fifteen cells coupled up.

Mr. Sperry: I understand that this is vulcanized.

Prof. Crocker: Yes, as a unit. The cells and conduits are all vulcanized together. There is nothing loose about it. It is one integral mass.

Mr. Sperry: Of course a great many attempts have been made to improve storage batteries by a number of engineers and a great many attempts have been made to make these connections out through the side of the cell as in the case of the connections before us. Sulphuric acid is used here the same as is used in storage batteries and really the exterior liquid is more violent than sulphuric acid; attempts to bring conductors from storage cells out to the side has resulted disastrously heretofore. as you will recall in storage batteries that are successful, these conductors have to be brought out from the top. The seepage, creeping and leakage are so extremely corrosive that it has always been found to be impracticable.

President Hering: I can answer one question of Mr. Sperry's. I think he will find that the corrosion of the positive terminal of an accumulator takes place when the battery is being charged. It is the oxidation that corrodes those terminals. In these pri-

mary batteries, however, they are not recharged in place, therefore the same tendency to oxidation of the positive terminals does not exist. As for the resistance of those connecting columns of liquids, Mr. Sperry will find, if he will make the calculation, that a long column of liquid of small cross section has a very high resistance. I have made that calculation myself and was surprised to see how little leakage there would be through that resistance.

PROF. CROCKER: The internal resistance is .013 ohm per cell, which is an exceedingly low figure for a primary battery. I have seen results even less than that.

MR. SPERRY: Of course that is high as compared with the internal resistance of a storage battery of same capacity.

PROF. CROCKER: Well, is it?

MR. SPERRY: It compares quite favorably in point of size to a storage battery of the same capacity and also as to bulk.

PROF. CROCKER: The discharge rate is higher.

MR. TUCKER: For isolated plants the preparation of the battery fluid would seem to present some difficulties. In the case of storage batteries the preparation of the electrolyte is troublesome enough, and here we have the addition of the bichromate.

I would like to know what the local action amounts to in a battery of a certain weight or capacity.

PROF. CROCKER: The theoretical weight of zinc that should have been consumed to give one-third of a horse power-hour is 0.392 lbs. Actually the consumption was 0.444 lbs. Some of the tests we have made show a better result. I think you can easily get 88 per cent. zinc efficiency. In other words the local action is 12 per cent. That is not excessive of course, but it would be better if reduced.

MR TUCKER: Would that 12 per cent. loss take place if the battery was unused?

PROF. CROCKER: Yes, I think it would. On the other hand, lowering the discharge rate does not seem to reduce the efficiency of the output.

*A paper read at the Tenth General Meeting of the American Electrochemical Society, held in New York, N. Y., October 8, 1906, President Hering in the chair.*

# ULTRA-VIOLET LIGHT IN THE LABORATORY AND IN PRACTICE.

By Charles Baskerville.

Lenard[1] in 1900 noted that ultra-violet light may ozonize oxygen. The source of this light of short wave-length used by him was a spark-gap, the light being transmitted through quartz. It could be intercepted by sheets of mica.

Three years later, Goldstein[2], with liquid air, condensed ozone produced outside of Geissler tubes. Unless the glass were permeable to the ultra-violet rays, that is, composed largely of quartz, no ozone was obtained.

The next year Warburg[3] found that during the silent electric discharge, the familiar method for producing ozone in a Siemens' tube, ultra-violet light and cathode rays were obtained and the production of ozone might be attributed to these rays.

This *savant* in collaboration with Regener[4] used a differential ozonometer with quartz capillary and learned that not alone was an ozonizing influence exercised by the ultra-violet light, but as well a de-ozonizing.

Clement[5] has shown that ozone is rapidly destroyed by increase in temperature. Fischer and Braehmer[6] confirmed this, and by using a quartz mercury-lamp for the source of the ultra-violet light demonstrated beyond question the ozonization of oxygen under that influence. Manganese glass exposed a few hours to this ultra-violet light acquires the coloration observed in it after long exposure to sun light.

These writers put forward the suggestion that ozone is formed

[1] Ann. Phys., *1*, 486.
[2] Berichte, *36*, 3042.
[3] Ann. Phys. *13*, 475.
[4] Sitzungsber. Preuss. Akad. d. Wiss., 1904, 1228.
[5] Ann. Phys., *14*, 334 (1904).
[6] Berichte, *38*, 2633 (1905).

in the higher portions of the atmosphere by the unabsorbed ultra-violet rays, sinks to lower regions and is decomposed by oxidizable substances.

Regener[7], has determined that ultra-violet light rays of wave-length smaller than 200 $\mu\mu$ produce ozone, whereas the rays with wave-length of about 257 $\mu\mu$ or higher decompose it. Therefore, we have a double action of the ultra-violet light. The apparently spontaneous de-ozonization is similar to that of the influence of the elevation of temperature. An interesting and wide field of investigation is thus opened up for the study of the action of ultra-violet light of different wavelengths. We have been using a mixture of reagents, as it were.

Regener has also shown that the ultra-violet rays of small wave-length decompose ammonia, nitrogen monoxide and nitrogen dioxide. Many chemical effects now known are manifested under the influence of the silent electric discharge. Nearly all gases and mixtures of gases, except the noble ones, are capable of at least one chemical reaction under its influence. It has been almost demonstrated that the silent discharge is similar to the action of ultra-violet light and when that is definitely accomplished our knowledge of photographic chemical phenomena will have acquired a much broader field.

Ramsay and Spencer[8] have recently studied some chemical and electrical changes induced by ultra-violet light. An electroscope charged positively is discharged by ultra-violet light. When negatively charged this does not occur. A conclusion was drawn from the work, which indicates that elements, and compounds, when illuminated by ultra-violet light, discharge corpuscles.

It has long been known that willemite (zinc orthosilicate) phosphoresces under the influence of ultra-violet light. If there be one thing in science that is attractive, it is the seeing of the invisible. Ever since, and even before the days when Cascariolo in 1602 discovered what is now called "Canton's phosphorus," people have been actively interested in the phenomena of phosphorescence and fluorescence. It may be said to have eventuated in the discovery of radium.

[7] Ann. Phys., *20*, 1033 (1906).
[8] Chem. News, *94*, 77 (1906).

Many natural substances have been found which glow in the dark under various influences. In the course of a prolonged study of the elaborate Morgan-Tiffany collections of gems and minerals in the American Museum of Natural History, Kunz and the writer exposed thirteen thousand specimens to ultra-violet rays. The light used was obtained by sparking a high tension current among iron terminals in the lamp devised by Piffard. Only one or two of the many interesting observations will be noted here.

First, in examining the spodumenes a new pink one obtained from California phosphoresced, showing a marked difference from the other varieties. This was proved to be new and the beautiful gem has been named *Kunzite* in honor of my colleague in the investigations.

Second. One of the most phosphorescent minerals observed was colemanite. In the examination I was surprised to note that every mineral obtained from Mono Lake phosphoresced. These minerals obtained from other sources varied very much in their conduct. These do not crystallize alike, hence the phenomenon cannot be explained on that basis. They vary widely in their chemical composition as may be seen from this list.

Colemanite, $Ca_2B_6O_{11}.5H_2O$
Glauberite, $Na_2SO_4.CaSO_4$
Borax, $Na_2B_4O_7.IoH_2O$
Polyhalite, $2CaSO_4.MgSO_4.K_2SO_4.2H_2O$.
Halite, $NaCl$
Celestite, $SrSO_4$
Thenardite, $Na_2SO_4$
Gypsum, $CaSO_4.2H_2O$
Hanksite, $4Na_2SO_4.Na_2CO_3$
Northupite, $MgCO_3.Na_2CO_3.NaCl$
Pirssonite, $CaCO_3.Na_2CO_3.2H_2O$.

Investigators of phosphorescent substances prepared in the laboratory have proved the need of some impurity in the material or the presence of something other than that looked upon as necessary to produce the actual chemical compound. This has been done in the case of the phosphorescent sulphides. Mr. Bourgougon of this laboratory has prepared willemite, pure zinc orthosilicate,

and it does not phosphoresce, but with the addition of manganese and other metallic oxides in small amounts, splendid artificial willemite has been made. Humphreys has found the yttria earths in the fluorspars, and I have noted that chlorophane, the most responsive of all of these fluorides, contains nearly one per cent. of the yttria earths.

Some one has said that prophecy is the most gratuitious mistake, but to my mind there must be something not recognized in the ordinary analyses of those minerals from Mono Lake, and from them may come an element for a vacant place in Mendelejeff's table.

The artificial wollastonite (calcium metasilicate), and the pseudo-wollastonite made by Day and Allen show a marked difference under the influence of the ultra-violet light. The pseudo-wollastonite glows in the dark and may be readily separated from the normal preparation.

On account of the brilliant response willemite gives to the ultra-violet light, at my suggestion it has been placed in the concentrating rooms of the New Jersey Zinc Co., where large quantities of that mineral are prepared for the furnace daily. A perfect control is thus had over the waste in the tailings.

We frequently use the lamp in the laboratory for the examination of precipitates, before and after burning. I am inclined to think it will serve a greater purpose as has been indicated.

---

## DISCUSSION.

Dr. W. D. Bancroft: Regener has shown that light with a wave-length between 200 $\mu\mu$ and 300 $\mu\mu$ destroys ozone, while light of less than 200 $\mu\mu$ changes oxygen into ozone. Does Dr. Baskerville know of any screen or solution which will absorb the wave-lengths of 200-300 $\mu\mu$ while permitting the shorter wave-lengths to pass? If we had such a light-filter, it would be possible to obtain more ozone commercially with the same expenditure of power.

I understand that, with the ultra-microscope, it has been possible to see the particles of sodium set free when rock salt is colored by the cathode rays. Can any similar phenomenon be

observed with any of the transparent, fluorescing or phosphorescing minerals?

Mr. E. A. Sperry: Mr. Hammer, who has had considerable experience in this field, and has lectured upon the subject before the Society, is present, and I suggest that he be asked to address the meeting.

Mr. William J. Hammer: I have been much interested in Dr. Baskerville's lecture and wish to take the liberty of calling attention to several matters which occur to me. Referring to the willemite screens which Dr. Baskerville has shown, I wish to state that my friend, Mr. W. S. Andrews, made such screens, employing both natural and artificial willemite, a long time ago, and I have in my possession several such screens which he gave me several years ago. I wish to take exception to Dr. Baskerville's statement regarding the specimen of willemite which he has shown as having been the first specimen stimulated by the rays of radium. I believe I was the first person to take up actively in this country the work with radium and I had the honor of delivering a lecture upon radium and other radio-active substances, ultra-violet light, etc., at the first joint meeting of the American Electrochemical Society and the American Institute of Electrical Engineers, as far back as April 17th, 1903, and at about this time I had made up various mixtures of radium with phosphorescent and fluorescent substances, using willemite, sulphides of zinc, calcium and many other substances. I had the pleasure of showing certain of these mixtures to Dr. Baskerville at my laboratory before he and Mr. Kunz took up this work, and I have therefore been interested to note that Mr. Kunz has recently taken out a couple of patents on mixtures of radium with phosphorescent and fluorescent substances. A combination of radium and sulphide of zinc which I secured at the Curie Laboratory was shown at my lecture before this society as well as many phosphorescent and fluorescent substances which I stimulated with both the mercury arc lamp and the ultra-violet light produced by Dr. Piffard's form of lamp, which is a modification of the Görl, Bang, Finsen, and other lamps made abroad. Dr. Piffard's lamp is a very useful device, but it might be stated that the study of minerals with the spark gap is some forty years old and anyone desiring to study willemite and other substances with

ultra-violet light can do so most successfully by using iron wire as the electrodes of the secondary of an induction coil, shunting or bridging the spark gap with a Leyden jar or condenser. The mercury arc is an exceedingly suitable stimulant for phosphorescent substances, but a note of warning should be given to those utilizing lamps of quartz such as the Heraeus lamp, as the ultra-violet light, which penetrates glass very slightly, passes readily through the quartz tube, and I know of two persons who have been incapacitated for months after examining the quartz tubes for only a very short space of time. I am interested in what Dr. Baskerville says about the importance attached to the examination of the minerals produced by the New Jersey Zinc Co., as I offered, nearly three years ago, to take my ultra-violet outfit into their mines at Franklin and make a study of the willemite and other deposits in the mine, but at that time the matter seemed to be of little interest to them, although I was given permission to visit the mine with a view of procuring specimens of willemite, of which I have a large collection.

Several years ago, in common with others, I made some interesting investigations into the opacity of minerals to various rays, especially those of Radium and Roentgen Rays, and in connection with experiments in imparting radioactivity to various substances, made an experiment which may prove of interest. I placed eight small fish of four varieties and of about the same size in each of two small aquariums, placed about thirty feet apart, the aquariums were filled with fresh water at the same time and from the same source. I then dropped some sealed glass tubes containing radium in one aquarium, and subsequently all the fish died which had been thus exposed to the radium, whereas all the fish in the other aquarium lived. I then took two gold fish which had become radioactive as they swam about, and after drying, laid them upon an X-ray plate previously covered by two sealed envelopes, one black and one orange, which were totally opaque to light rays, and the dead fish made excellent radiographs of themselves by means of their stored-up radioactivity. I have the fish and their radiograph mounted and framed, still in my possession.

Mr. Baskerville: I know of no screen which accomplishes such light-filtration asked about by Mr. Bancroft. I wish I did.

With reference to Mr. Hammer's remark, that I have a patent on mixtures of radium salts and certain phosphorescent bodies, I beg leave to say that no patent has ever been issued to me.

I may be in error with regard to the sample of willemite referred to. If so, I am only too ready to correct it.

With regard to willemite screens, will say that Mr. Andrews has made screens from our preparations, which we were glad to supply him. The previously reported artificial willemite one hears of in Europe, a sample of which is in my possession, is not synthetic willemite. The European product shows the presence of soluble salts, *i. e.,* chlorides or sulphates. Ours was made from purified zinc and silicon oxides, in molecular proportions, for the ortho-silicate. Variable amounts of manganese and other oxides were added to different preparations, with consequent different behavior.

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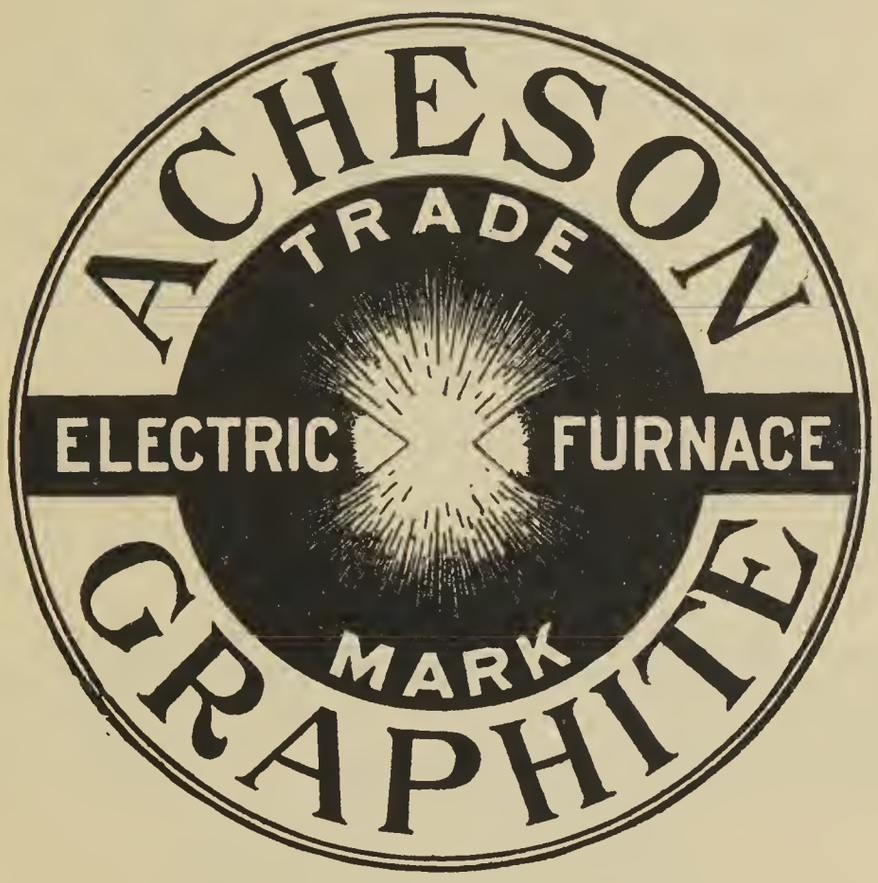


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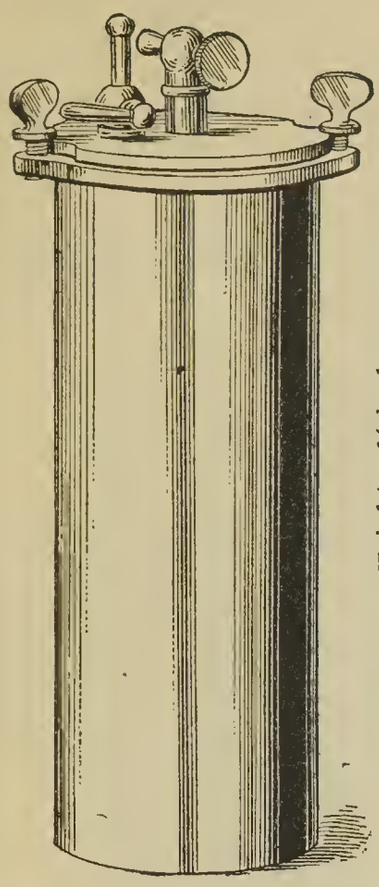

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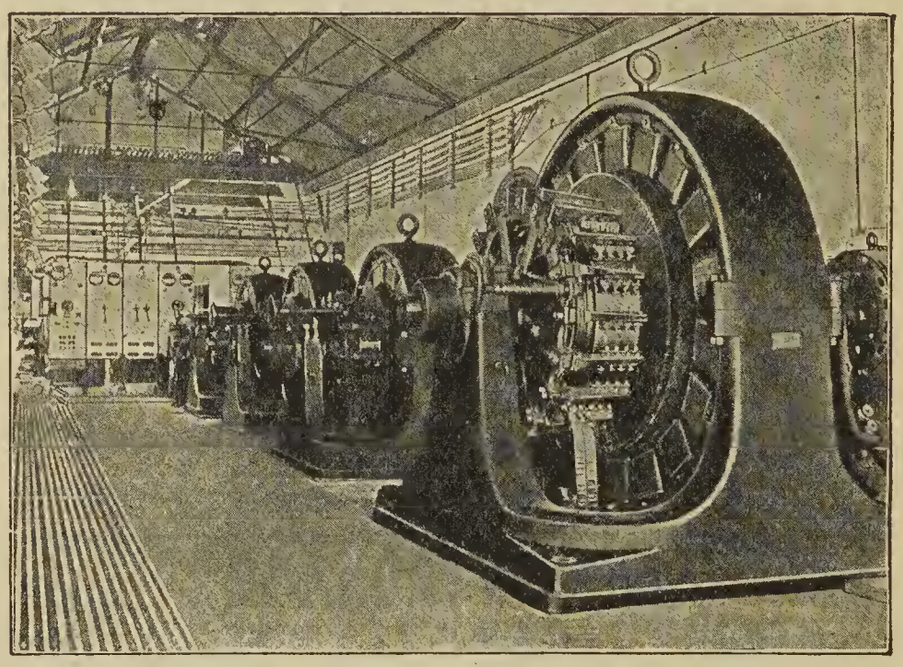

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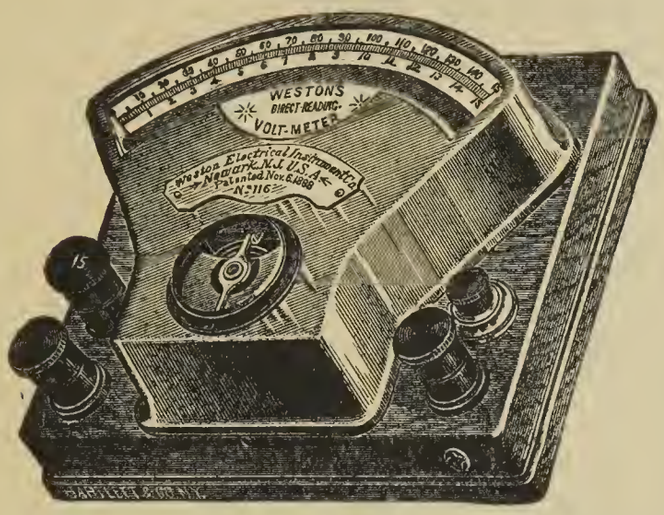


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